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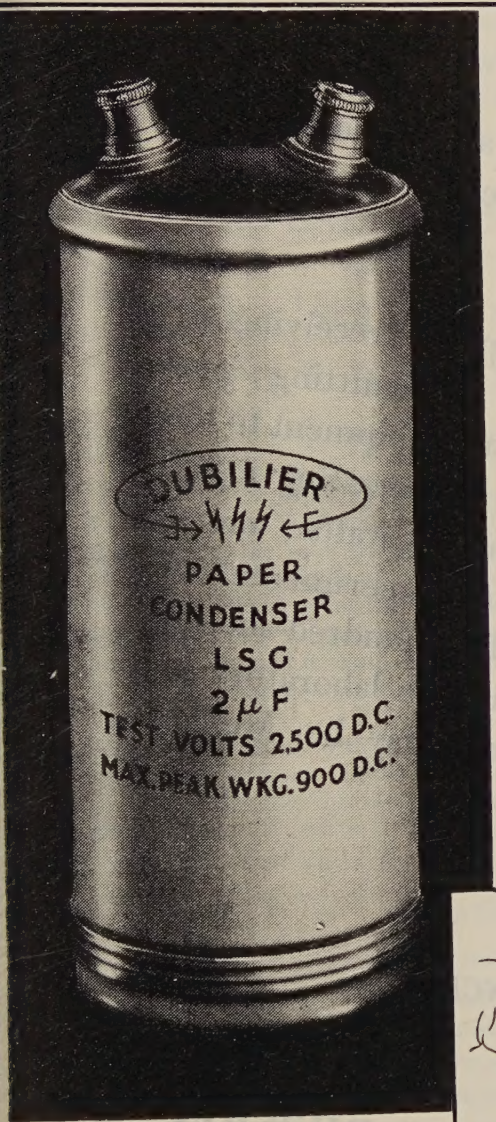

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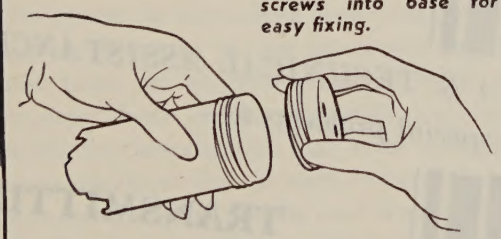

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ELECTRO-ENDOSMOSIS AND ELECTROLYTIC WATER-TRANSPORT

PART 3. SOLUTIONS OF COPPER SALTS

BY H. C. HEPBURN, PH.D., Birkbeck College

Received June 26, 1933

ABSTRACT. This paper gives the results of measurements of the liquid-transport produced by passing an electric current through aqueous solutions of cupric chloride and of cupric nitrate, the solution in each case being symmetrically divided by means of a parchment-paper diaphragm perpendicular to the direction of the flow of electricity. The results are considered in relation to data obtained previously by the author in the case of solutions of copper sulphate; and the electro-endosmotic effect of the parchment-paper diaphragm is discussed in terms of the influence of the electrical charge of the diaphragm and of the thickness of the electrical double layer formed at the interface diaphragm-aqueous solution.

The results obtained with the solutions of cupric chloride show that the direction of liquid transport is reversed in the case of the more concentrated solutions, and evidence is adduced suggesting that this reversal is attributable to the effect of the electrolytic water-transport.

§ 1. INTRODUCTION

THE author has previously* investigated the electrolytic water-transport in the case of copper-sulphate solutions by means of the parchment-paper diaphragm method. At the same time, the electro-endosmotic effect of the parchment-paper diaphragm and its dependence on the electrolyte concentration were examined. In the present work the investigation has been extended to solutions of cupric chloride and of cupric nitrate, so that the work embraces solutions of the cupric salts of the three common mineral acids. In the case of cupric nitrate, however, it was not found practicable to obtain satisfactory results with solutions of concentrations exceeding 0·0464-normal owing to disturbances introduced by a chemical action which accompanied the electrolysis.

* *Proc. Phys. Soc.* **43**, 524 (1931); *ibid.* **44**, 267 (1932).

The electro-endosmotic effect of the parchment-paper diaphragm, which becomes prominent in the case of the dilute solutions, is discussed in the light of experimental data obtained previously by the author and by other workers. The influence of (*a*) the electrical charge of the diaphragm, and of (*b*) the thickness of the electrical double layer (formed at the interface diaphragm-aqueous solution) is considered by means of a method proposed by the author in former papers*.

The results obtained with the solutions of cupric chloride show that the direction of liquid transport is reversed in the case of the more concentrated solutions; and evidence is adduced suggesting that this reversal is attributable to the effect of the electrolytic water-transport.

§ 2. EXPERIMENTAL

The apparatus employed, which was similar to that described by the author in a former paper†, consisted of two electrode chambers (one open to the air and the other closed) separated by a diaphragm of parchment paper. The liquid-transport across the diaphragm, when an electric field was applied at the electrodes, was determined, as in the previous work, by observing the movement of the liquid thread in a capillary tube attached to the closed electrode chamber.

The apparatus was immersed in an electrically heated water bath with a thermostatic device arranged to provide a temperature-control within the limits $18 \pm 0{\cdot}1^\circ$ C.; and to avoid thermometric effects no heat was supplied to the tank immediately before or during the course of the flow-measurements. A higher working temperature ($22{\cdot}0^\circ$ C.) was necessitated in the case of 0·0464-normal cupric-nitrate solution, as the room temperature during the measurement with this solution exceeded 18° C. Control experiments have indicated, however, that the variation in the liquid-transport per faraday over the temperature range $18{\cdot}0^\circ$ C. to $22{\cdot}0^\circ$ C. is less than the limit of experimental error (between 1 and 2 per cent).

As in the previous work, reversible copper electrodes were employed. A potential-difference of 20 V. was applied at the electrodes in the case of solutions of concentrations 0·1-normal and less, but at higher concentrations it was found desirable to adopt a lower voltage (6 V.) in order to minimize the possibility of disturbances arising from electrode reactions.

Determinations of liquid-transport were carried out with the solutions in order of increasing concentration. At the completion of the series of measurements with the cupric-chloride solutions the parchment-paper diaphragm was changed, and a further series of measurements made with the cupric-nitrate solutions. The employment of an entirely fresh diaphragm for each series of measurements obviates the difficulty, as the author‡ has pointed out, of removing by a washing process the last traces of adsorbed electrolyte from the diaphragm.

The experimental method adopted to measure the rate of liquid-transport differed slightly from that previously followed by the author. The meniscus, after

* *Proc. Phys. Soc.* **38**, 363 (1926); *ibid.* **39**, 99 (1927).
† *Ibid.* **43**, 525 (1931).
‡ *J. Chem. Soc.* 3163 (1927).

traversing approximately 1 cm. of the capillary tube, was timed over a further 1 cm. of the tube (the time for the half cm. being taken also for purposes of checking), the potential-difference at the electrodes being applied in a given direction. The direction of the applied potential-difference was reversed when the meniscus had traversed a further 1 cm. of the tube, the meniscus, moving in the reverse direction, being again timed over the selected 1 cm. length.

If the initial movement is towards the end of the capillary remote from the apparatus, v_f, the liquid-transport per faraday, is given by the following expression: v_f

$$v_f = [(1/T_1 - 1/T_s)\,(1/I_1)\,(0{\cdot}00973)\,(96{,}540)] - [C] \qquad \ldots\ldots(1),$$

where T_1 (sec.) is the observed time of liquid-transport per cm., T_s (sec.) the time of gravitational movement per cm. outward, I_1 (A.) the mean current through the diaphragm, 0·00973 the volume of the capillary in cm^3 per cm. and C the correction for the heating effect of the current* expressed in cm^3 per faraday. The corresponding expression for the liquid-transport on reversal is as follows: T_1, T_s I_1 C

$$v_f = [(1/T_2 + 1/T_s)\,(1/I_2)\,(0{\cdot}00973)\,(96{,}540)] + [C] \qquad \ldots\ldots(2),$$

where T_2, I_2 correspond with T_1, I_1. T_2, I_2

Adding (1) and (2), we obtain the following expression for v_f:

$$v_f = \frac{K_1}{2}\left(\frac{1}{T_1 I_1} + \frac{1}{T_2 I_2}\right) + \frac{K_1}{2T_s}\left(\frac{1}{I_2} - \frac{1}{I_1}\right) \qquad \ldots\ldots(3),$$

K_1 being the product 0·00973 × 96,540. The second term on the right-hand side of equation (3) may in general be neglected, the correction introduced in the present measurements being considerably less than 1 per cent except in the case of 0·5-normal (correction 11 per cent) and 1·0-normal (correction 8 per cent) cupric-chloride solutions where the values of I_1 and I_2 (see table 1) are somewhat divergent. Thus a precise measurement of the gravitational movement is in general unnecessary, and the correction for the heating effect of the current is eliminated†. K_1

Control experiments showed that it was not essential in all cases to change the solution before making the reverse measurement of the liquid-transport, but this step was found desirable with the more concentrated solutions (e.g. those of 0·1-normal concentration and greater concentrations) in order to minimize the possibility of disturbances arising from reactions at the electrodes and from concentration-changes accompanying prolonged electrolysis.

Cupric-chloride solutions. Solutions of concentrations ranging from 0·0005-normal to 1-normal were employed, all of them being prepared by dilution from standard 2-normal solution. Analytical reagent cupric chloride was employed to prepare the standard solution, the concentration which was checked by the potassium-iodide, sodium-thiosulphate method of volumetric estimation. The sodium-thiosulphate solution employed in this estimation was standardized against a solution of analytical-reagent copper sulphate.

Preliminary observations showed a rapid diminution in the current, soon after completion of the circuit, in the case of solutions of 0·2-normal concentration and

* See *Proc. Phys. Soc.* **43**, 529 (1931).

† The author previously employed equation (1) to determine v_f.

greater concentrations; a similar effect was obtained when the diaphragm was removed from the apparatus. The effect was accompanied by the deposition on the anode of an insoluble substance (probably an insoluble basic salt of copper formed by a secondary action at the electrode), the effective surface area of the electrode (and consequently the magnitude of the current also) diminishing progressively as deposition occurred. After the initial stage, however, the rate of current-diminution became less rapid; and sufficiently steady current-values were obtained, when a potential difference of 6 V. was applied at the electrodes, to enable measurements of liquid-transport to be made. No material variations in the current-values and in the rates of liquid-transport were observed in the case of solutions of concentrations 0·1-normal and less.

Cupric-nitrate solutions. A standard solution of approximately 1-normal concentration was made up, Kahlbaum's "purest" cupric nitrate being employed. The precise concentration of the standard solution was found by volumetric estimation to be 0·928-normal, and the solutions employed were prepared by dilution from this solution.

In the case of solutions of concentrations greater than 0·0464-normal, evolution of gases from the cathode was observed, the free nitric acid present (in consequence of hydrolysis of the solution) apparently reacting with the deposited copper and liberating nitrogen and certain oxides of nitrogen. The electrode reaction referred to appeared to introduce irregularities in the rate of liquid-transport, and no satisfactory results were obtained in the case of solutions of concentrations greater than 0·0464-normal; at the lower concentrations (0·000464-normal to 0·0464-normal), however, control measurements indicated practically uniform rates of liquid-transport.

§ 3. RESULTS AND CONCLUSIONS

The experimental results are given in tables 1 and 2.

The liquid-transport v_f in cm.^{3}/faraday is calculated by means of equation (3)*. I_m I_m (column 9 of tables 1 and 2) is the mean of I_1 and I_2. The values given for the specific conductivity λ have been obtained by large-scale graphical interpolation from the data of A. Heydweiller† and of H. C. Jones‡.

v_f is shown in the tables as positive where the direction of liquid-transport is from anode to cathode.

The liquid-transport per faraday. The relation between the liquid-transport v_f per faraday and the electrolyte dilution is shown graphically in figure 1; the curve for solutions of copper sulphate has been added for purposes of comparison. In each case the values of v_f, over the dilution range 20 to 1000, lie satisfactorily on a smooth curve; and the value for dilution 2000 (or dilution 2155 in the case of the cupric-nitrate solutions) lies above the extension of the curve. The values of v_f

* See p. 757.

† Landolt-Börnstein, *Tabellen*, p. 1086 (1923).

‡ *Ibid.* p. 1092. Temperature coefficients have been computed by the author from the data of Heydweiller and Jones in order to obtain values of λ appropriate to a temperature of 18° C.

in the case of copper-sulphate solutions are higher than those relating to solutions of cupric chloride and of cupric nitrate. In the two latter cases the values lie fairly closely together, but certain differences are exhibited (see p. 763). No linear law, similar to that relating to the case of a powdered-glass diaphragm and copper-sulphate solutions of dilutions 10 to 200*, or to the case of a parchment-paper diaphragm and potassium-chloride solutions of dilutions 10 to 100†, is applicable to any of the present cases.

Table 1. Cupric-chloride solutions

Concentration (gm.-equiv./litre)	Current I_1 (A.)	Current I_2 (A.)	Time T_1 (sec.)	Time T_2 (sec.)	Liquid-transport v_f (cm.^{3}/faraday)	Applied potential difference (V.)	Specific conductivity λ (reciprocal ohms)	$I_m/\lambda V$
0·0005	0·000832	0·000800	710·0	1130·7	1318	20·5	0·0000625	0·637
0·001	0·001503	0·001536	476·5	738·3	1069	20·5	0·0001134	0·653
0·002	0·002947	0·002965	327·6	512·5	796	20·5	0·0002162	0·667
0·005	0·00724	0·00721	262·5	366·4	425	20·4	0·000518	0·684
0·01	0·01396	0·01398	245·2	351·7	233	20·5	0·001007	0·677
0·02	0·02649	0·02659	254·4	456·2	108	20·4	0·001934	0·673
0·05	0·0621	0·0608	519·2	2250	18·0	20·3	0·004495	0·674
0·1	0·1175	0·1150	− 750	− 232·5	− 22·9	20·5	0·00833	0·681
0·2	0·0256	0·02635	27000	− 680·5	− 25·6	6·15	0·01544	0·273
0·5	0·0151	0·0092	3440	−1198	− 29·9	6·19	0·03355	0·058
1·0	0·0169	0·0107	2122	− 900	− 32·8	6·13	0·0569	0·039

Table 2. Cupric-nitrate solutions

Concentration (gm.-equiv./litre)	Current I_1 (A.)	Current I_2 (A.)	Time T_1 (sec.)	Time T_2 (sec.)	Liquid-transport v_f (cm.^{3}/faraday)	Applied potential difference (V.)	Specific conductivity λ (reciprocal ohms)	$I_m/\lambda V$
0·000464	0·000665	0·000665	838·5	1308·8	1381	20·4	0·0000518	0·629
0·000928	0·001364	0·001393	607·0	696·0	1050	20·4	0·0001028	0·658
0·001856	0·002720	0·002767	406·7	456·8	795	20·4	0·0002027	0·663
0·00464	0·00669	0·00680	301·4	368·6	420	20·4	0·0004918	0·673
0·00928	0·01317	0·01341	248·6	316·9	254	20·4	0·000948	0·687
0·01856	0·02522	0·2548	216·6	306·6	146	20·3	0·001815	0·688
0·0464	0·0637	0·0621	272·4	1310·0	32·8	20·2	0·004422	0·704

The reversal of liquid-transport with cupric-chloride solutions and the apparent discontinuity in the curve between dilutions 10 and 20 (see figure 1 *A*) are discussed on pp. 763, 764.

The electro-endosmotic effect of the parchment-paper diaphragm. In order to examine the electro-endosmotic effect of the parchment-paper diaphragm in the light of the classical theory‡, it is necessary to obtain values for the electro-endos-

* H. C. Hepburn, *Proc. Phys. Soc.* **39**, 99 (1927).

† H. Remy, *Z. Electrochem.* **29**, 365 (1923).

‡ Helmholtz, *Wied. Ann.* **7**, 337 (1879). See also M. v. Smoluchowski's monograph on electro-endosmosis in Graetz's *Handbuch der Elektrizität und des Magnetismus*, Bd. 2 (2), p. 366 (1914).

v motic liquid-transport v produced by the application across the diaphragm of a constant potential difference. Subject to certain limitations discussed by the author in a former paper*, v is given by the following expression:

$$v = K_2 (v_f - H) \lambda \qquad \text{.....(4),}$$

v_f, H, λ, K_2 where v_f is the observed liquid-transport per faraday, H the electrolytic water-transport per faraday, λ the specific conductivity of the electrolyte solution, and K_2 a constant.

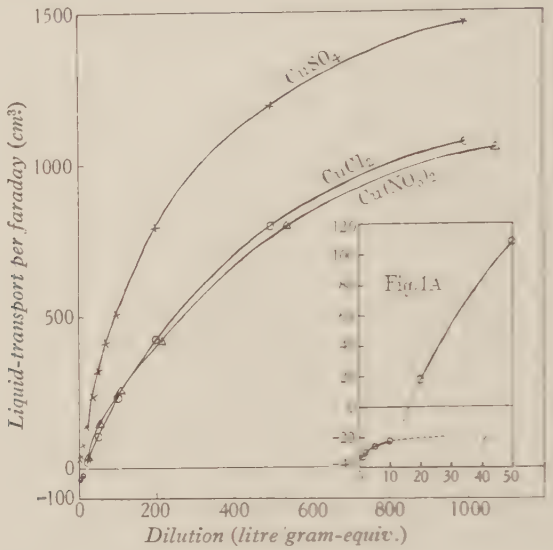

Figure 1. Liquid-transport per faraday. An enlargement of the lower part of the $CuCl_2$ curve appears in figure 1*A*.

I_m, V Equation (4) implies a proportionality between the specific conductivity λ and the mean current I_m flowing through the diaphragm when a given voltage V is applied at the electrodes. Values of $I_m \lambda V$ are given in tables 1 and 2, column 9, and are seen to be practically constant over the concentration range 0·005-normal to 0·1-normal in the case of cupric-chloride solutions, and over the concentration range 0·00464-normal to 0·01856-normal in the case of cupric-nitrate solutions. The somewhat lower values of $I_m \lambda V$ in the case of concentrations less than 0·005-normal (cupric chloride) or less than 0·00464-normal (cupric nitrate) suggest a diaphragm polarization effect†; the lower values in the case of 0·2-normal, 0·5-normal and 1·0-normal cupric-chloride solutions, however, appear to be due mainly to the effect referred to on pp. 757, 758 and not to diaphragm-polarization.

H appears to be negative in the case of cupric-chloride solutions (see p. 764), interpolation of the curve of figure 3, which shows the relation between H and concentration, giving values for H which range from $-18{\cdot}7$ cm³ in the case of 0·0005-normal solution to $-22{\cdot}9$ cm³ in the case of 0·1-normal solution. The values

* *Proc. Phys. Soc.* **43**, 534 (1931).
† *Ibid.* **44**, 267 (1932).

of H thus obtained have been employed to compute the expression $(v_f - H)\lambda$, which is plotted against concentration in figure 2. It may be pointed out, however, that if a constant value for H is assumed over the concentration range 0·0005-normal to 0·1-normal no material error is introduced. In the case of copper-sulphate solutions, the evidence adduced by the author* in a former paper suggests that H is here positive and approximately constant at concentrations not greater than 1-normal. The expression for v/K_2, equation (4), appropriate to this case, viz. $(v_f - 29{\cdot}3)\lambda$, is also plotted in figure 2 for purposes of comparison.

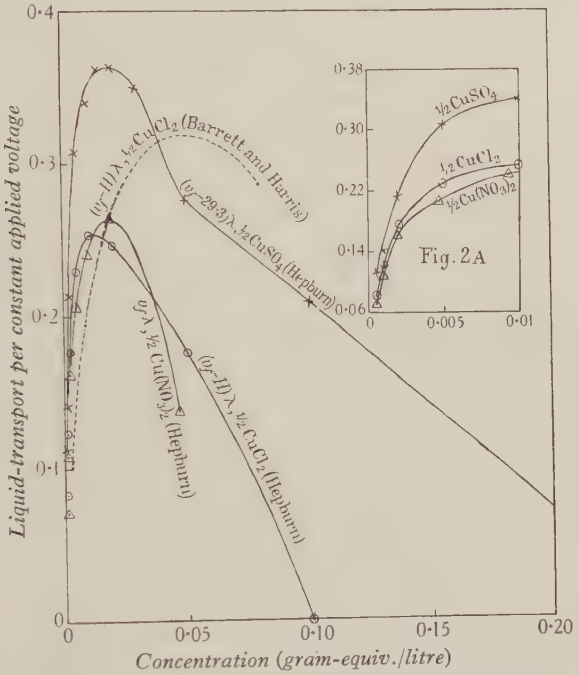

Figure 2. Liquid-transport per constant applied voltage across the diaphragm. Figure 2*A* shows the rising branches of the curves in greater detail.

Values of H are not available in the case of the cupric-nitrate solutions, the curve given in figure 2 for these solutions representing the expression $v_f\lambda$; i.e. no correction is applied for the electrolytic water-transport. If, however, a correction is applied of the same magnitude as that appropriate to the cupric-chloride solutions or to the copper-sulphate solutions, the order of the rising branches of the three curves remains unchanged up to concentration 0·005-normal.

The values of $(v_f - H)\lambda$ (or of $v_f\lambda$ in the case of the cupric-nitrate solutions) for concentrations 0·002-normal (or 0·001856-normal in the case of the cupric-nitrate solutions) and less lie in each case on the lower part of the rising branch of the curve, the possible disturbances produced by diaphragm polarization (see p. 760) apparently having little effect on the general form of the curves.

* *Proc. Phys. Soc.* **43**, 533 (1931).

Variations in the form of the (v, concentration) curve obtained with a given solution appear to arise when different specimens of parchment paper are employed as diaphragms, e.g. the curve obtained from the data of J. O. W. Barrett and A. B. Harris* for solutions of cupric chloride differs from that given by the author's results; see figure 2. These variations are probably attributable to differences in the electrolyte content, texture, etc., of the parchment paper employed; all the diaphragms employed in the present work were therefore cut from the same sample of parchment paper so as to ensure that the results obtained with different solutions should be strictly comparable.

The curves of figure 2 show that v, in each case, increases initially with increasing concentration, attains a maximum value, and then regularly decreases. In order to trace the factors which contribute to these maxima, it is convenient to examine the
e relation between v and the mean surface density e of the charge on the walls of the parchment-paper diaphragm channels. This relation, according to the classical theory, is as follows:

$$v = (K_3/\eta)\,\delta.e \qquad \ldots\ldots(5),$$

δ where δ is the effective thickness of the electrical double layer at the interface
K_3, η diaphragm-solution, K_3 is a constant, and η is the viscosity coefficient, which may be regarded as a constant in the case of the dilute solutions here considered.

It has not been found practicable, owing to experimental and other difficulties, to examine the dependence of δ and e on the electrolyte concentration in the case of the parchment-paper discs employed in the present work; but the author† has devised a method enabling such an examination to be made in the case of electro-endosmotic measurements with a powdered-glass diaphragm. This method, suitably modified, has since been employed by H. B. Bull and R. A. Gortner‡ in the case of streaming-potential determinations with a cellulose diaphragm. The author obtained maxima in the (v, concentration) curves§, similar to those found in the present work (figure 2), in the case of the electro-endosmotic flow of aqueous solutions of potassium chloride, hydrochloric acid and barium chloride through powdered glass. There were also maxima in the (δ, concentration) curves, but the diaphragm charge e increased with increasing concentration except in the case of solutions of potassium chloride, where a slight initial decrease followed by a regular increase appeared.
ζ The results of Bull and Gortner are expressed in terms of ζ, the interfacial potential-difference of the electrical double layer, which is usually taken as proportional to v in the case of dilute solutions. Bull and Gortner find maxima in the case of the (ζ, concentration) curves relating to aqueous solutions of potassium chloride, sodium chloride, potassium carbonate and potassium sulphate. The corresponding (δ, concentration) curves indicate that δ decreases continuously with increasing concentration, except in the case of solutions of sodium chloride and potassium

* *Z. Elektrochem.* **18**, 221 (1912).

† *Proc. Phys. Soc.* **38**, 363 (1926); *ibid.* **39**, 99 (1927).

‡ *J. Phys. Chem.* **35**, 309 (1931).

§ Values were plotted of ζ, the interfacial potential-difference of the electrical double layer, which was taken as proportional to v.

sulphate, where slight maxima appear. The maxima in the (ζ, concentration) curves were accompanied in all cases by regular increase in the diaphragm charge, this result corresponding with that obtained by the author with the powdered-glass diaphragms. Proceeding by analogy, it thus seems probable that the maxima in the (v, concentration) curves, obtained in the present work with the parchment-paper diaphragms, arise from the simultaneous effect of increasing diaphragm charge and decreasing thickness of the electrical double layer, modified to some extent by initial increase in the latter quantity. In this connexion, it may be observed that cellulose appears to bear a closer relation to parchment paper than does powdered glass, and in the cases recorded by Bull and Gortner for cellulose the modifying factor referred to is not of great effect.

The curves of figure 2, taking the values of v at concentration 0·005-normal, indicate the following order of the anions:

$$SO_4 > Cl > NO_3.$$

This order, which follows that of the well-known lyotropic series*, suggests also the order of adsorbability of the anions by the parchment-paper diaphragm. Such adsorption, which would tend to increase the initial negative charge of the diaphragm†, would be consistent with the charging effect indicated by the (e, concentration) curves relating to the cellulose and powdered-glass diaphragms. The series holds although the concentrations are expressed in gram-equivalents. The effect of the SO_4'' ion in producing initial increase in the value of v, as compared with the respective and approximately equal effects of the Cl' and NO_3' ions, the common ion in each case being Cu'', thus appears to be greater than would be explained by the influence of valency alone.

The electrolytic water-transport. H. Remy‡ and J. Baborovsky§, in the light of experimental evidence obtained with a considerable number of solutions, have concluded that the electro-endosmotic effect of a parchment-paper diaphragm may be neglected in the case of solutions of normal concentration. The liquid-transport obtained with normal cupric-chloride solution would thus be attributable wholly to electrolytic transference, i.e. v_f, table 1, would represent the electrolytic water-transport. The values of v_f over the concentration range 1·0-normal to 0·1-normal lie on a smooth curve, figure 3, the direction of liquid flow over this range of concentrations being opposite to that relating to concentrations 0·05-normal and less. The values of v_f for the latter series of concentrations also plot into a smooth curve, which appears, however, to be entirely unconnected with the continuation of the curve of figure 3. It seems evident from figure 2 that the electro-endosmotic effect of the parchment-paper diaphragm is considerably less pronounced with cupric-chloride solutions than with copper-sulphate solutions, and in the latter

* See H. Freundlich, *Colloid and Capillary Chemistry*, pp. 57, 58 (1926).

† The direction of electro-endosmotic flow, i.e. from anode to cathode, indicates that the diaphragm is negatively charged.

‡ *Trans. Far. Soc.* **23**, 383–385 (1927). See also H. C. Hepburn, *Proc. Phys. Soc.* **43**, 531–532 (1931).

§ *Z. Phys. Chem.* **129**, 129 (1927); *Coll. Czech. Chem. Comm.* **1**, 315 (1929).

case the evidence adduced by the author in a former paper* suggests that the effect referred to becomes negligible at a concentration slightly greater than 0·2-normal. It therefore appears probable that the curve of figure 3, representing v_f for cupric-chloride solutions of concentrations normal to 0·1-normal, may be accepted as giving an approximate indication of the electrolytic water-transport over this range of concentrations.

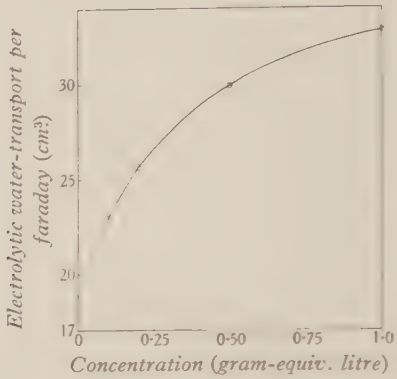

Figure 3. Electrolytic water-transport with solutions of cupric chloride.

Following the above, the reversal of liquid flow obtained with solutions of cupric chloride (i.e. a chloride of a bivalent cation) would be attributed to the effect of the electrolytic water-transport. In this connexion it is significant that the direction of liquid flow after reversal, i.e. from cathode to anode, is the same as that found by H. Remy and E. Manegold† for all cases examined of normal solutions of chlorides of bivalent cations‡; on the other hand, the direction of liquid flow found for the cases of normal solutions of chlorides of univalent cations was from anode to cathode. The result appears to be due mainly to the greater proportion of Cl′ ions to cations in the case of solutions with bivalent cations, thus resulting in a preponderating electrolytic water-transport towards the anode in the latter case.

The values obtained by Remy and Manegold§ for the electrolytic water-transport x (mol faraday) in the case of normal solutions of magnesium chloride, calcium chloride, strontium chloride and barium chloride (all chlorides of bivalent cations), viz. 0·08, 0·20, 0·97 and 1·23 respectively, are somewhat lower than the value 1·82‖ obtained by the author for normal cupric-chloride solution.

§ 4. ACKNOWLEDGMENT

The author desires to thank Prof. A. Griffiths for facilities provided and for the interest he has shown in this investigation.

* *Proc. Phys. Soc.* **43**, 534 (1931).
† *Z. Phys. Chem.* **118**, 161 (1925).
‡ See H. Remy, *Trans. Far. Soc.* **23**, 382 (1927).
§ *Loc. cit.* ‖ $x = v_f/18{\cdot}02$, $v_f = 32{\cdot}8$, table 1.

621.317.738

A NEW CAPACITY-METER

By W. L. BECK, A.M.I.E.E.

Received July 24, 1933.

ABSTRACT. A new form of capacity-meter is described which simplifies the comparison of capacities over a wide range of values.

§ 1. THE RECTIFIER METHOD

The measurement of capacity in the new meter is based on the comparison of the impedance of the condenser under test with a calibrated standard impedance in a differential rectifier circuit described below, the balance being indicated by a d.-c. galvanometer.

In the circuit shown in figure 1 an unknown condenser C_1 and a standard condenser C_2 are each connected in series with a rectifier of bridge type, and placed in parallel on the same a.-c. supply. It can readily be seen that in this circuit there will be no deflection of the differential galvanometer G by the d.-c. currents of the rectifier bridges when the impedance of C_1 is equal to that of C_2. This assumes that the two rectifiers are of equal efficiency, and that the leakage currents through the condensers are negligible in comparison with their displacement currents, an assumption which may usually be made.

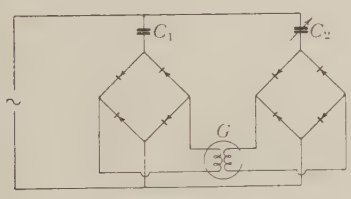

Figure 1.

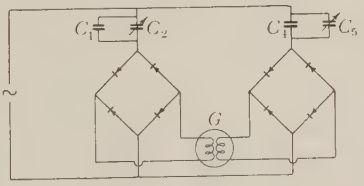

Figure 2.

The high sensitivity obtained with a d.-c. galvanometer renders this type of bridge valuable for the comparison of air-dielectric condensers. The effect of leakage and inequality of the two rectifiers may be eliminated by the use of the substitution arrangement shown in figure 2.

By a modification of the circuit it is possible to dispense with the differential galvanometer. One method is to connect the d.-c. circuits of the bridge rectifiers in direct opposition through a suitable galvanometer. With this arrangement, however, it is necessary to connect a resistance in shunt across each rectifier to protect it from damage. A more sensitive arrangement is shown in figure 3. In this circuit each bridge rectifier is replaced by two series-connected rectifier

elements, and the double-wave rectifiers thus formed are connected in opposition through a simple moving-coil galvanometer. The a.-c. lead from each corner of the bridge is connected through a stopping condenser C_s to eliminate the short-circuit across the galvanometer.

§ 2. THE RECTIFIER CAPACITY-METER

A variable plate condenser with air dielectric forms a convenient continuously adjustable standard of capacity for this bridge. Its range, however, is limited to capacities of the order of a few hundred $\mu\mu$F. This difficulty has been overcome in the capacity-meter by connecting the condenser under test to the rectifier bridge through a multi-ratio single-wound current-transformer, in order to provide a number of ranges of capacity.

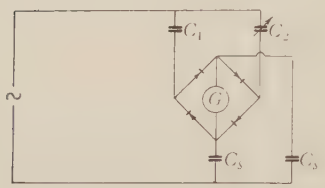

Figure 3.

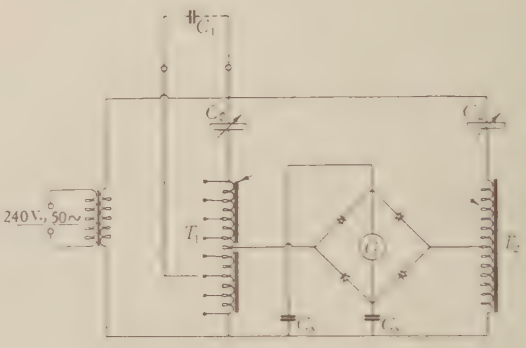

Figure 4.

The schematic circuit diagram of the instrument is shown in figure 4. The rectifier bridge is used in the same form as in figure 3 and the capacity C_1 under test is connected to the bridge through the tapped transformer T_1. The standard condenser C_2 has a maximum capacity of approximately 1200 $\mu\mu$F., and is connected to the bridge by a second transformer T_2. This steps up the current which is applied to the rectifier bridge in the ratio of approximately 3 : 1 so that the rectifiers work over a better part of their characteristic; this arrangement gives increased sensitivity and reduces the temperature coefficient of the rectifiers. To equalize the circuit, T_1 is connected to the bridge from a tapping which provides a similar ratio.

A small variable condenser C_3 is connected between the end of T_1 and the supply, to provide a convenient means of balancing the minimum capacity of C_2, and allows the capacity scale to be calibrated down to zero. This condenser also forms a convenient means of compensating for the capacity of the leads connecting the meter to the capacity under test. Thus if a preliminary balance is made by adjusting C_3 with one of the leads disconnected close to the test condenser, while the index of C_2 is on the zero of the scale, the capacity of the leads will be eliminated from any subsequent measurement.

The meter is fed from the supply mains by an insulating transformer which steps down the voltage across the condenser under test to approximately 100. A number of protective resistances which are not shown in figure 4 are introduced into the supply circuit by a switch mechanically coupled to the range switch, which selects the tapping on the transformer T_1. These protect the instrument from damage in the event of the leads to C_1 being short circuited.

The instrument as manufactured has a scale approximately 300 mm. in length, and is calibrated from zero to 1·2 μF. Eight ranges are provided having multiplying factors of 0·001, 0·005, 0·01, 0·05, 0·1, 0·5, 1 and 2. Thus it is possible to cover a range of capacities from 5 $\mu\mu$F. to 2·4 μF. Balance is indicated by a convenient self-contained d.-c. pointer galvanometer, which also indicates the direction of the out of balance capacity. The sensitivity is sufficient to show a departure from balance of one part in 1000 when the instrument is working over the upper part of the calibrated scale. The meter is normally arranged for an a.-c. supply voltage of 240 volts at 50 cycles per second, and its calibration is not changed by more than 0·3 per cent by a change in voltage of 25 per cent. In its present form, the calibration is accurate to at least 0·5 per cent of full scale reading, or 1 per cent of any reading above 0·2 on the scale.

The operation of the meter is extremely simple, and the use of a pointer moving over the calibrated scale renders the instrument particularly suitable for use under industrial conditions. For repetition work, maximum and minimum limits can readily be marked on the scale, making it unnecessary for the operator to read the actual value of the capacity.

The range of capacities on this model have been chosen to cover the normal requirements of industry. It is possible, however, to construct other models having ranges above or below these values. Thus, for instance, a special instrument could be arranged to give full scale for 100 $\mu\mu$F., or the upper end of the range could be extended to 12 or 24 μF.

§ 3. ACKNOWLEDGMENT

The instrument is being manufactured by the Cambridge Instrument Company Ltd., to whom the writer is indebted for permission to publish this paper.

546.212 : 548.7

THE MOLECULAR STRUCTURE OF ICE AND LIQUID WATER

By E. L. KINSEY and O. L. SPONSLER, University of California at Los Angeles

Communicated by Sir William Bragg, F.R.S., July 25, 1933

ABSTRACT. In §§ 1 to 6 a lattice, new so far as the hydrogen-ion positions are concerned, and based on the oxygen positions previously determined by Barnes, is proposed for ice. The structure contains the units H^- and $H^-_3O_2$, the latter built so that three hydrogen ions lie at the corners of an equilateral triangle in the plane midway between, and perpendicular to, the line of centres of the two oxygen ions. It consists of neutral chains extending parallel to the c axis and arranged about one another in a manner consistent with the symmetry and oxygen-position requirements. Large polarization effects arise, and reasons are given why a lattice in which they are produced is preferred to a co-ordination structure in which they are absent. The structure provides dihydrol as the polymer occurring in both ice and water, evidence for whose existence has arisen from various sources; and by means of a reasonable postulate in regard to the stability of the $H^-_3O_2$ ion in the crystal, and in clusters of dihydrol occurring in the liquid, it allows a qualitative explanation to be given of many of the abnormal properties of water and ice.

In § 7 the model is used to calculate the angle θ between the c axis and the line joining an oxygen with a hydrogen ion in the $H^-_3O_2$ unit, both when the unit is within the lattice and when it is within dihydrol regarded as isolated. The calculations are not exact, but indicate that $\theta = 30°$ to within a few degrees when the unit is in the lattice. The effect of the lattice on θ is shown to be small (several degrees), whereas the effect on the polarization of the oxygen is large and is such as to increase it nearly threefold over its value for isolated dihydrol. Use is made of this fact in accounting for the stability of dihydrol in the crystal lattice.

§ 1. INTRODUCTION

The abnormal properties of ice and water have received the attention of various workers for many years*. Many of the anomalies such as the abnormal temperature variation of the specific heat of the liquid, the lowering of the freezing-point with pressure, and the existence of a point of maximum density, have been explained by the hypothesis which supposes the liquid to be a mixture of simple H_2O molecules and polymers of these, a mixture that freezes into a solid in which the highest polymers appear as units. In order to explain the facts for the liquid the polymers have been assumed to be in temperature equilibrium with the simple molecules, to occupy more space than their constituent simple parts separately, and to require the addition of energy to dissociate them. Their existence has also been regarded, until fairly recently†, as

* See H. M. Chadwell, *Chem. Rev.* 4, 375 (1927) for review of the literature and bibliography.

† G. G. Longinescu, *Chem. Rev.* 6, 381 (1929).

affording a reason why water fails to obey many of the empirical relations connecting molecular weights with boiling-points, freezing-points and surface tension, relations which are obeyed by the so-called normal liquids.

Recent spectroscopic studies of liquid water have offered evidence for the existence of polymers of a different nature. The discovery through the Raman effect of bands which vanish with increasing temperature and with the addition of an acid*, the occurrence of infra-red absorption bands in the liquid and solid states which are absent in the vapour†, and the abnormal shifts of other bands which occur upon the addition of an acid‡ offer significant support for existence of aggregates, aggregates which may be called molecules in the strictest sense. To this evidence should be added the results of X-ray diffraction studies in liquid water§, although their complete interpretation is not yet clear.

Suggestions have been made from time to time in regard to the nature of the polymers, but nothing definite seems to be known. For the liquid, mono-, di- and tri-hydrol have been assumed to exist, but any direct evidence for these assumptions has been lacking. For ice a suggestion has been made that it is composed of trihydrol, but so far no critical examination of the available X-ray data has been carried out to see whether such a unit can exist. In fact, the only lattice which has been proposed for ice as yet is ionic in character and does not contain a complex unit of any sort.

It is the purpose of this paper to show that on the basis of the present X-ray data on the crystal structure of ice a new lattice can be proposed which will account for the existence of a polymer, and which with the use of a reasonable postulate in regard to stability will also account, qualitatively, for many of the abnormal properties of both ice and water.

§ 2. THE BARNES LATTICE

The lattice positions of the diffracting centres in ice under normal conditions have been determined by Barnes‖ in such a thorough piece of work that there can be no doubt that the lattice given by him is correct, so far as the positions of the oxygen ions are concerned. Reasons are given by him for supposing the centres to be oxygen ions, and they are so considered here. The oxygen lattice has the hexagonal or trigonal symmetry of the space groups D^4_{6h} or D^4_{3h}. There are four oxygens in a unit cell; each has a trigonal axis through it parallel to the singular axis, and each is at the centre of a tetrahedron whose corners are formed by other oxygen ions. The black spheres in figures 1 and 2 represent such a lattice. If a linear chain of these parallel to the c axis is examined, it will be seen to consist of ions spaced by alternate long and short intervals.

*. E. H. L. Meyer, *Phys. Z.* **30**, 170 (1929); E. L. Kinsey, *Phys. Rev.* **35**, 284 (1930).
† J. W. Ellis, *Phys. Rev.* **38**, 693 (1931).
‡ E. L. Kinsey and J. W. Ellis, *Phys. Rev.* **36**, 603 (1930).
§ G. W. Stewart, *Phys. Rev.* **37**, 9 (1931); H. H. Meyer, *Ann. d. Phys.* **5**, **6**, 701 (1930).
‖ W. H. Barnes, *Proc. R.S.* A, **125**, 670 (1929).

The X-ray data furnished no information in regard to the positions of the hydrogens, and therefore Barnes was forced to assume positions for them which not only preserved the symmetry of the lattice but appeared reasonable. The lattice selected was a co-ordination one in which a hydrogen ion was placed at the mid point of each line joining a central oxygen ion with one at the corners of the surrounding tetrahedron. This choice brings one hydrogen ion into the middle of the short interval between oxygen ions along the c axis. An alternative arrangement which had to be considered, since the X-ray analysis failed to distinguish between the space groups D_{6h}^{4} and D_{3h}^{4}, was obtained by rotating the three hydrogen ions lying in the basal planes about the c axis, so that they moved off the lines joining the two adjacent oxygen ions. But Barnes considered the first arrangement to be the more probable.

§ 3. OBJECTIONS TO A PURE CO-ORDINATION LATTICE

There appear to be various objections to a lattice of the type just described. In the first place, so far as we know, substances known to have a co-ordination lattice, and whose liquids have been studied, form electrically-conducting liquids. The alkali halides are typical examples. On the other hand, the crystal structures of substances which form non-conducting liquids seem to be of the non-coordination type. It therefore does not appear likely that a non-conducting liquid such as water will freeze into a pure co-ordination lattice in which the units are ions that are extremely difficult to separate.

In the second place, the melting-points of substances having co-ordination lattices are high, in most cases hundreds of degrees higher than the melting-point of ice. It is true that those for the halogen hydrides are low, but these substances in many respects are quite different from the salt-like bodies which possess co-ordination lattices. They are known to be poor conductors as liquids, and, for the reasons being set forth for water, they too may not possess co-ordination lattices.

In the third place considerations arise which lead one to suspect that a lattice will be formed in which there will be strong polarization. Hund*, in a discussion of the cadmium-iodide type of lattice (layer lattice) in which the iodine ion is strongly polarized because it is unsymmetrically surrounded by cadmium ions, sets forth the conditions which favour the existence of polarization. He shows that for the cadmium-iodide type the lattice energy is larger for the layer lattice than for a co-ordination structure, and that the energy increases with the ratio $\alpha\, r^3$, where α is the polarizability and r is the ionic distance. Thus, layer lattices are more stable energetically than co-ordination ones in cases where α is large and r is small. In the ice lattice, for reasonable positions of the hydrogen ions, the oxygen-oxygen distances require very small oxygen-hydrogen distances. In the Barnes lattice, for example, if the oxygen-ion radius is taken as 1·32 A.†, that for the hydrogen ion becomes 0·08 A., and if the value 1·40 Å. of Pauling‡ is taken, no room at all is

* F. Hund, *Z. f. Phys.* **34**, 833 (1925).
† See V. M. Goldschmidt, *Trans. Faraday Soc.* **25**, 253 (1929).
‡ L. Pauling, *Proc. R.S.* A, **114**, 181 (1927).

left for the proton. Such a close approach of two ions is not known for any lattice yet examined, so far as the authors know. The lithium cation is next smallest with a radius of 0·8 Å. It is evident that the slightest departure from a co-ordination arrangement, where such small distances are involved, will result in strong polarizing fields. In addition, the oxygen ion itself has a substantial polarizability, so that the two conditions necessary for the formation of some type of "layer or chain" lattice are certainly present.

In the fourth place, a consideration of the series Ag_2O, Cu_2O, Li_2O, H_2O shows that the large difference in properties between the first three and water will require some fundamental change in the type of lattice. The first three have cubic co-ordination lattices. Table 1* indicates the extent of the dissimilarity expected.

Table 1

	Radius ratio	Radius sum
Ag_2O	0·855	2·45
Cu_2O	0·727	2·28
Li_2O	0·591	2·16
H_2O (Barnes's lattice)	0·061	1·40

Through suggestions of this sort we have been led to look for a lattice more like the layer type than the co-ordination type, i.e. for one in which strong polarization can occur.

§ 4. THE PROPOSED NEW ICE LATTICE

A consideration of Barnes's oxygen lattice will show that another arrangement of hydrogen ions, different from any of those mentioned by him, is possible. If the hydrogen ions are placed in the symmetry plane which passes midway between the oxygen ions and is perpendicular to the *c* axis, in such a way that three of them form an equilateral triangle whose centre lies at the mid point of the short oxygen-interval and upon one of the *c* axis chains, and a fourth, to be designated as the "singular hydrogen ion," is placed on the *c* axis chain at the mid point of the long oxygen-interval, all of the symmetry requirements of the lattice are still obeyed, and the proper number of hydrogen ions is provided. Figures 1 and 2 represent a model built in this way, in which the black and white spheres represent oxygen and hydrogen ions respectively. The three hydrogen ions which form triangles in the basal planes will be referred to as type *T* hydrogen ions. Planes of symmetry parallel to the basal plane and trigonal axes parallel to the *c* axis are still preserved. Equally spaced basal planes may be drawn such that every alternate one contains hydrogen ions, and the others locate two oxygen planes close together, as can be seen in figure 2.

A more significant view is provided by considering a chain of oxygen ions parallel to the *c* axis. If the double-pyramidal group H_3O_2 is regarded as a unit, any one chain is seen to be a column of such groups and H^+ ions alternately spaced. Moreover if the group $H^-{}_3O_2.H^+$ is regarded as a dipole it is seen to be surrounded

laterally by three others pointing oppositely, while along the c axis the dipoles are strung end to end. The whole lattice may be described as a cluster of linear chains of dipole dihydrol units. But it is not safe to carry this view too far, for it is obvious that because of its symmetrical position half way between two $H^{-}{}_3O_2$ groups, a

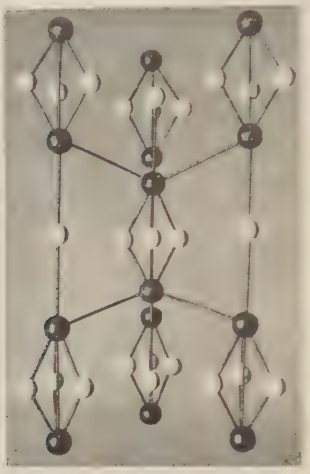

Figure 1 *A*.

Figure 1 *B*.

Figure 1. Four c axis chains of proposed ice lattice. *A*, view of model perpendicular to c axis; *B*, view of model along c axis. White and black spheres represent centres of hydrogen and oxygen ions respectively.

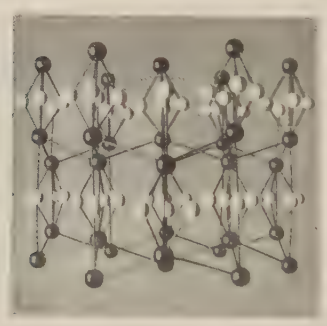

Figure 2 *A*.

Figure 2 *B*.

Figure 2. Extended model of ice lattice. *A*, basal planes; *B*, hexagonal structure.

singular hydrogen ion cannot be associated definitely with any one of them, at least in the lattice at equilibrium. However, in what follows, it will be convenient on occasion to regard the dihydrol group ($H^{+}.H_3O_2$) as a unit whose properties may be examined.

It is evident that because of the unsymmetrical environment of hydrogens the oxygen ions are now in electric fields directed along the c axis toward the singular hydrogen, and that polarization of the ions in this direction will result.

§ 5. POSTULATE OF A LIMIT OF STABLE APPROACH FOR THE SINGULAR HYDROGEN

It is not possible to fix through symmetry restrictions alone either the orientation of the triangle of three hydrogens or its size, but through certain assumptions in regard to the crystal forces involved some idea of the order of magnitude of the angle θ between the c axis and the line from an oxygen to a hydrogen of the triangle, as well as of the orientation of the triangle, may be obtained. These considerations are given in § 7. They show that an angle within a few degrees of 30° is reasonable. They also show that the orientation of the triangle given in figure 1*A* is probably the stable one. If these results are assumed, the oxygen-singular-hydrogen distance of 2·32 Å. is about 1·4 times the oxygen-*T*-hydrogen distance of 1·61 Å. If the *T* hydrogens are regarded as spheres resting upon the surface of an oxygen ion of radius 1·40 Å. (or 1·32 Å.), the radius of the hydrogen ion becomes about 0·21 Å. (or 0·29 Å.). The singular hydrogen ion is then not in contact with an oxygen ion, but is held in equilibrium away from it by electrostatic forces which are due partly to the ionic charges of the $H^{-}{}_{3}O_{2}$ group and partly to the polarization of the surrounding oxygen ions. The interval between the surfaces of the two ions is 0·71 Å. When the dihydrol unit is removed from the lattice these forces of repulsion become smaller*, for the effect of the neighbouring ions is to increase the oxygen polarization and hence to increase these repulsive forces. If they are weakened the singular hydrogen will approach the $H^{-}{}_{3}O_{2}$ group. The absence of evidence for the existence of dihydrol in the vapour state indicates that its stability in the solid and liquid depends upon a repulsive force sufficient to maintain a minimum singular-hydrogen-H_3O_2 distance of approach. We have been led, therefore, to make the following postulate. *A critical distance of approach between the singular hydrogen and* H_3O_2 *groups exists such that when the approach is smaller, the dihydrol unit is unstable and spontaneously dissociates into two simple* H_2O *molecules.* Stability of the unit in the crystal is produced by increased polarization forces which result from the fields of the surrounding ions; and these fields maintain the singular hydrogen at distances from the $H^{-}{}_{3}O_{2}$ group larger than the critical distance of approach. Electric fields are present in liquid water also, so that if the same unit exists there (and from the optical evidence it is reasonable to suppose that it does†) its stability is maintained by large polarization in the same way.

The ability of the postulate to provide those properties for polymers which it has always been necessary to assume in order to account qualitatively for some of the abnormalities of water is immediately evident. It will be of interest to consider briefly some of these abnormalities.

* Cf. § 7.

† J. W. Ellis, *Phys. Rev.* **38**, 693 (1931).

§ 6. SOME PROPERTIES OF ICE AND WATER FROM THE POINT OF VIEW OF THE PROPOSED LATTICE

Since the lattice is rendered unstable by any factors which cause too close an approach of the units along the *c* axis, increased pressure should produce a lowering of the lattice melting-point. Thus, the lattice provides for this well-known property of ice. Melting may be regarded as a destruction of the lattice due, primarily, to too close an approach of the singular hydrogen and H_3O_2 groups, resulting in a liquid which is a mixture of mono- and di-hydrol in temperature equilibrium.

The occurrence of a point of maximum density may be explained in the usual way. As the temperature rises from 0° an increase in dissociation of the more voluminous dihydrols into the more compact monohydrols will arise superposed upon a decrease in density caused by the increased temperature motion. These opposing effects will result in a point of maximum density which, according to the model, should shift to lower temperatures as the pressure is increased. This shift is another well-known behaviour of liquid water*.

The increase in compressibility of ice, which within certain limits occurs instead of the usual decrease as the pressure is increased*, can also be accounted for. Under those pressures for which the dihydrol lattice is stable, closer approach of the units along the *c* axis weakens the crystal repulsive forces, since unstable positions are being approached. The form of the potential-energy curve postulated for the dihydrol group, regarded as a diatomic molecule in the crystal lattice, serves to show this effect, figure 3. The compressibility is large in the regions near the limits of stability.

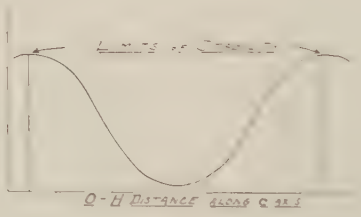

Figure 3.

Under sufficiently high pressures the lattice should disintegrate whatever the temperature. That ice behaves in this way is well known from Bridgman's work*. But the phenomena are not simple, as is shown by the existence of the many different modifications of ice. What is significant is that at the highest pressures all the properties of ice become normal, a point which Bridgman has emphasized. From the present point of view we may regard this as due to a transformation by stages from the dihydrol chain type of lattice to one completely regular in its behaviour, perhaps to one of co-ordination type such as Barnes suggested.

It should be mentioned also that the existence of a minimum in the specific-heat curve for water, and its displacement by pressure to lower temperatures, are

* P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.* **47**, 441 (1911–12).

accounted for in Nernst's usual way, since the dihydrol discussed here requires energy to dissociate it in the lattice.

There are other properties which it is profitable to consider from this point of view, but since they have to do with absorption and Raman scattering in water and acid mixtures they will be discussed elsewhere.

§ 7. CALCULATIONS

To obtain some idea of the probable equilibrium configuration of the H_3O_2 anion in the crystal lattice, it is convenient to treat the group as isolated, and then to determine the modifications which arise when it is introduced into the lattice. Three types of field are recognized as being effective, namely electrostatic fields due to the ionic charges, polarization fields due to the polarization of the oxygen ions, and repulsive fields, regarded as non-electrical, acting between the hydrogen ions and oxygen ions. For simplicity the calculation will at first involve only the ionic and repulsive forces between oxygen and hydrogen ions. A second calculation will take into account the polarization forces together with the effect of the lattice.

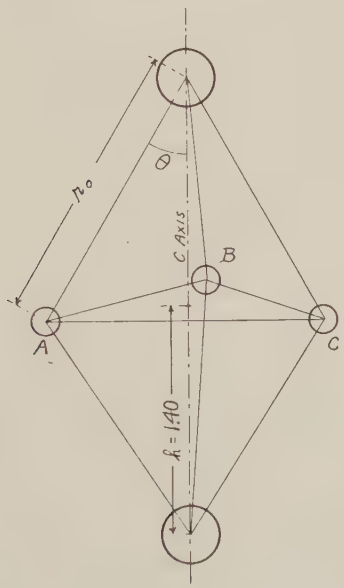

Figure 4. $H^-{}_3O_2$ unit. Large circles represent oxygen ions, small circles hydrogen ions.

Calculation of the angle θ for the isolated $H^-{}_3O_2$ ion. Since at equilibrium the forces in the plane of the triangle ABC, figure 4, on any one hydrogen ion and directed toward the c axis vanish,

$$\frac{4e^2}{r_0^2}\sin\theta - F(r_0)\sin\theta - \frac{e^2}{2h^2\tan^2\theta\cos 30^\circ} = 0 \qquad \text{.....(1)},$$

where e is the electronic charge, $F(r_0)$ is the value of the repulsive force between hydrogen and oxygen ions at equilibrium, and the other symbols are as represented in the figure. e, $F(r_0)$ h, θ

Similarly, the forces along the c axis on an oxygen ion and directed toward the centre of the H_3O_2 group must vanish at equilibrium, giving

$$\frac{6e^2}{r_0^2}\cos\theta - \frac{e^2}{h^2} - 3F(r_0)\cos\theta = 0 \qquad \text{.....(2).}$$

From equations (1) and (2) a single equation for θ can be obtained:

$$6x^3 + 1 = \frac{\sqrt{3}\,x^3}{(1-x^2)^{3/2}} \qquad \text{.....(3),}$$

where $x = \cos\theta$. This may be solved by calculating the quantities

$$y_1 = \frac{\sqrt{3}\,x^3}{(1-x^2)^{3/2}} \quad \text{and} \quad y_2 = (6x^3 + 1),$$

and setting $y_1 = y_2$. From table 2, the solution is seen to be $\theta = 37°$.

Table 2

θ	y_1	y_2	$y_2 - y_1$
30°	9·16	4·90	− 4·54
31	8·00	4·78	− 3·22
32	7·17	4·66	− 2·51
33	6·31	4·54	− 1·86
34	5·64	4·42	− 1·22
35	4·98	4·30	− 0·68
36	4·51	4·18	− 0·33
37	4·06	4·06	0·00
40	2·98	3·70	+ 0·72
50	1·03	3·29	+ 2·26

Effect of the lattice and the polarization forces. For the calculations which follow it is necessary to choose an orientation about the c axis for the triangle of three hydrogen ions. It has been assumed such that any side of the triangle is opposite one of the three surrounding chains, i.e., the vertices point symmetrically between any two of these chains. It is evident that this is one of two positions in which the torque on the H_3O_2 group, considered as a rigid body, is zero. A 60° rotation about the c axis gives the other position. Considering the effects of only the six immediately surrounding oxygens and the three surrounding singular hydrogens, it can be shown that the first position is stable and the second unstable. The calculation is the elementary one of considering the derivative of the torque in respect to the angle of orientation. Polarization fields have been neglected, so that the value of this result lies principally in indicating that the orientation used is the more likely of the two, for contributions to the torque due to polarization may be expected to be small.

The effect of the lattice and the polarization fields will be represented by two
c_1 terms; c_1e^2, the force on a hydrogen of the triangular group, in the plane of the
c_2 triangle and directed away from its centre; and c_2e^2, the force on an oxygen ion parallel to the c axis and directed away from the centre of the H_3O_2 group. These

must be subtracted from the left-hand sides of equations (1) and (2) respectively, which become

$$\frac{4e^2}{h^2}\cos^2\theta\sin\theta - F(r_0)\sin\theta - \frac{e^2}{2h^2\tan^2\theta\cos 30^\circ} - c_1e^2 = 0 \quad \text{.....(4)},$$

$$\frac{6e^2}{h^2}\cos^3\theta - \frac{e^2}{h^2} - 3F(r_0)\cos\theta - c_2e^2 = 0 \quad \text{.....(5)}.$$

In these equations r_0 has been replaced by $h/\cos\theta$. As before, a single equation may be obtained:

$$6x^3 + 1 = \frac{\sqrt{3}\,x^3}{(1-x^2)^{3/2}} + g \quad \text{.....(6)},$$

where

$$g = h^2(3c_1\cos\theta - c_2) \quad \text{.....(7)}. \qquad g$$

The solution is that value of x which satisfies

$$y_2 - y_1 = g \quad \text{.....(8)}.$$

The terms c_1 and c_2 contain (1) charge and polarization effects of the lattice, and (2) polarization effects of the $H^-{}_3O_2$ unit itself. So far as the angle θ is concerned the lattice effect is small (as is seen in what follows), so that its variation with θ has been disregarded. It has been calculated for a fixed angle of 36°. For the polarization effects in the unit, however, variations in θ become important. The terms are therefore functions of θ and are obtained for a series of θ values by calculating the inverse-square fields at an oxygen and a hydrogen of the triangle due to the surrounding charges and to the oxygen dipoles of polarizability α. The calculation is only approximate but has considered, in addition to the effect of a group's own chain, the effect of the first three and the next six surrounding chains. The smallness of this correction makes it of little value to extend the calculation further. Similar ions are arranged into sets, and the effect of each set is expressed by a series whose terms grow rapidly smaller. The effects neglected are of the order of a few per cent of the terms used.

For a field F at an oxygen dipole the terms become F

$$c_1 = 0{\cdot}0088 - (0{\cdot}0491 - M)\,\alpha F \quad \text{.....(9)},$$

$$c_2 = 0{\cdot}091 + (0{\cdot}0234 - N_1)\,\alpha F + 0{\cdot}158\,\alpha^2F^2 \quad \text{.....(10)},$$

where $M = 2{\cdot}90\sin\theta\cos^4\theta$, $N_1 = 1{\cdot}45(3\cos^2\theta - 1)\cos^3\theta$, and these terms represent the effect on a hydrogen ion of the polarization forces arising within the unit, and the effect of the triangle of three hydrogens on an oxygen dipole, respectively. The field F is given by M, N_1

$$F = K - 0{\cdot}255 - 0{\cdot}0507\,\alpha F \quad \text{.....(11)},$$

where $K = 1{\cdot}53\cos^3\theta$ and represents the effect of the triangle of three hydrogens. K

Values for these quantities are obtained by using Pauling's calculated value of the mol refraction, $R = 9{\cdot}88$, for the oxygen ion*. Since the polarizabilities of many ions in crystals have been found to be less than the values calculated for the free ions, we may regard this as an upper limit for α†.

* L. Pauling, *Proc. R.S.* A, **114**, 181 (1927).
† H. Heckman, *Z. f. Phys.* **31**, 219 (1925).

From the relation $R = \frac{4}{3}\pi N\alpha$, where N is Avogadro's number, the value

$$\alpha = 3{\cdot}9 \times 10^{-24}\ \text{cm}^3$$

is obtained. For convenience α is expressed in units of 10^{-24} cm^3, and the field F in units of 10^{16} e.s.u. These are the units used in equations (9), (10) and (11). Table 3 gives the values of the quantities c_1, c_2, g, $(y_2 - y_1)$, and F as functions of θ. c_1 and c_2 are expressed in units of 10^{16}.

Table 3

θ	c_1	c_2	g	$(y_2 - y_1)$	F
27°	—	—	—	− 7·85	—
28	− 2·03	− 2·35	− 5·97	− 6·34	0·67
29	− 1·95	− 2·12	− 5·86	− 5·18	0·65
30	− 1·84	− 1·87	− 5·72	− 4·54	0·62
31	− 1·83	− 1·64	− 5·97	− 3·22	0·59

Columns four and five show that for g to be equal to $(y_2 - y_1)$, which is the condition for equilibrium, θ must be, approximately, 28°.

The reduction from 37°, the angle for the isolated group, is due to the effect of the lattice and to the oxygen polarization. Since it is of interest to separate these two effects, calculations for θ, which include in every case the polarization effects, have been made for the following cases: (1) the $H^-{}_3O_2$ group isolated, (2) the group $H^-{}_3O_2$ on its chain and surrounded by three neighbouring chains, (3) the group on its chain surrounded by the first three and the next six chains, and (4) the group $(H_2O)_2$ isolated. The results are shown in table 4.

Table 4

	θ	F
$H^-{}_3O_2$ isolated	28°	0·54
$H^-{}_3O_2$ + 3 chains	27	0·78
$H^-{}_3O_2$ + 3 + 6 chains	28	0·67
$(H_2O)_2$ isolated	31	0·24

By comparison of the first three rows of the table, the effect of the lattice on θ is seen to be negligible. The polarizing field F, however, exhibits a greater variation. Rows three and four show that when the dihydrol group, $(H_2O)_2$, is in the lattice, the field F approaches nearly three times the value of the field when the group is isolated. Further, a simple calculation, using Pauling's value of the polarizability, shows that the small value of F for the isolated dihydrol is not sufficient to prevent the singular hydrogen ion from approaching and actually resting upon the surface of the oxygen ion. The model, therefore, is in accord with the view presented in previous sections, that the oxygen-singular-hydrogen separation is maintained only by forces which arise within the lattice.

The effect of a non-electrical repulsive force between the two oxygen ions so far has been omitted. Since they are in contact if Pauling's value for the oxygen ion

radius is assumed, it is reasonable to suppose that such a force exists. If it does, it will affect the term c_2 only, and in such a way as to make it larger; and since this term is always negative its absolute value will be smaller. This will make the absolute value of g larger, as a glance at equation (7) shows, and hence will decrease the angle θ below 28°.

We may conclude, therefore, that an upper limit of 37° for θ is reasonable, and that the angle is more likely to be nearer 30° than 37°.

§ 8. CONCLUSION

The foregoing remarks show that a lattice may be assumed for ice which accounts in a very reasonable way for the existence of a complex group in both the solid and the liquid states. The solid is regarded as a lattice of two types of ions, the H cation and the complex double pyramidal anion H_3O_2, which form neutral chains parallel to the c axis. At the melting-point, a temperature lower than that required to cause the ionic dissociation $H^+.H^-{}_3O_2 \rightarrow H^+ + H^-{}_3O_2$, a re-arrangement of hydrogen ions, of such a character as to produce large numbers of single water molecules, occurs. These will exist in temperature equilibrium with the remaining dihydrol, which is prevented from dissociating by the fields that are still present in the liquid. It cannot be supposed, however, that the true state of the liquid is completely represented by so simple a picture. Clusters of variable size of the two types of molecules no doubt are the mobile units. In fact, the X-ray diffraction phenomena point to the existence of a kind of orderly clustering which may follow the crystalline arrangement. The significance of the view presented lies in the fact that a structure of ice can be assumed which is compatible with the X-ray data, admits of the existence of a polymer, and can provide for many of the abnormalities exhibited by the substance.

535.338:546.812

THE BAND SPECTRUM OF TIN OXIDE

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ABSTRACT. The spectrum of SnO has been produced by a flame source which offers considerable advantages over the arc previously used by Mahanti, and the spectrum has also been obtained in absorption. Experimental evidence has been secured confirming that the emitting molecule is SnO. The vibrational analysis of Mahanti's *A* system has been extended to $v' = 8$, and approximate values of the vibrational constants have been calculated from the band-head data. The lower electronic level of this system has been shown to be the ground state. It is doubtful whether the so-called *B* and *C* systems actually exist as separate systems.

§ 1. INTRODUCTION

THE spectrum of tin oxide, SnO, consists of well-marked bands degraded to the red, and extends through the blue and near ultra-violet. The bands were observed by Eder and Valenta* in the oxy-coal-gas flame spectra of tin sulphide and tin chloride, and afterwards in the arc spectrum of metallic tin on carbon poles by Mahanti†. Mahanti measured the band heads on photographs of the tin arc in air, and arranged many of them in three systems which he designated *A*, *B* and *C*. The principal bands all fall into the *A* system, the *B* and *C* systems being only fragmentary.

The use of the arc, however, has the disadvantage that the accompanying line spectrum of tin and bands of CN and C_2 tend to obscure the oxide bands; and a further difficulty arises from the great extension of individual bands, due to the high temperature of the source, the tails of the stronger bands overlapping and covering the weaker heads.

The aim of the present investigation was to record the positions of the band heads as completely as possible by the use of a flame, and to extend the vibrational analysis of the spectrum.

§ 2. THE MOLECULE EMITTING THE SPECTRUM

Mahanti attributed the spectrum to the oxide molecule SnO, after eliminating the possibility of its being due to SnH or Sn_2. Analysis of the bands has shown that the molecule SnH must be ruled out, but some doubt was felt as to whether Sn_2 might not be the molecule concerned. Mahanti considered this improbable for two reasons: firstly, on account of the occurrence of the bands when tin salts were heated in the strongly oxidizing flame; and secondly because he saw no

* *Atlas Typischer Spektren.*

† *Z. f. Phys.* **68**, 114 (1931).

alternations of intensity in the lines of a given branch of those bands which he could observe under high dispersion. Such alternations would be visible if the molecule were symmetrical.

In the present work, however, the source has been a reducing flame of hydrogen containing stannic-chloride vapour. This flame contains a considerable quantity of metallic tin vapour, which will readily condense on any cold body held in the flame. The first reason given by Mahanti therefore carries little weight, as the spectrum is obtainable from both oxidizing and reducing flames.

As regards the alternations of intensity, careful examination of the (1, 0) and (2, 0) bands does suggest some such alternations in lines of the same branch, but the dispersion in the first order of the 10-ft. grating is not sufficient to make it quite certain that the variations are not due to overlapping.

It was therefore considered desirable to obtain further experimental evidence with regard to the molecule emitting these bands. Accordingly an enclosed arc chamber was set up, in which an arc could be maintained in gases other than air, at either atmospheric pressure or reduced pressures. Owing to the low melting-point of tin, solid rods of the metal could not be used in the usual way. The lower pole was an iron cup $2\frac{1}{2}$ cm. in diameter and containing the tin, which became molten when the arc was struck; while the upper pole was a hollow copper rod, cooled right up to the tip by running water. In operation, the copper became covered with a layer of tin condensed from the arc, so that copper lines were only faintly visible.

The characteristic bands were readily obtained when air was used in the arc chamber. After careful removal of all oxide from the poles, hydrogen was introduced into the chamber, but it was not found possible to obtain the bands in this gas although different pressures were used. Negative results were also obtained when nitrogen was used. It must therefore be considered extremely probable that SnO is the molecule concerned, since oxygen appears to be necessary for the production of the spectrum.

§ 3. THE LIGHT-SOURCE

The light-source first employed in the present work was a hydrogen flame burning in air at a silica jet. The hydrogen was taken from a cylinder and was passed through a Wolff's bottle containing anhydrous stannic chloride, $SnCl_4$. It was not necessary, or indeed desirable, actually to bubble the gas through the liquid, as a sufficient quantity of vapour became mixed with the hydrogen when this was simply passed over the surface of the liquid in the bottle.

The flame obtained in this way is bright blue in colour and has a faint yellow centre, presumably due to the emission of continuous radiation from heated particles of oxide in the solid state. In the outer parts of the flame the temperature is sufficiently high to vaporize the solid. In later experiments, made for the purpose of studying the absorption spectrum of the flame, nitrogen was mixed with the hydrogen to reduce the temperature, and it was then observed that the yellow

central portion rose through the outer blue region and appeared above the rest of the flame. Photographs of the flames with hydrogen alone and with hydrogen-nitrogen mixture are shown at (*g*), (*h*) in the plate.

These flames have a peculiar appearance and it is probable that an examination of their structure would yield useful information on the chemical changes involved in flame reactions*.

The flame spectrum obtained in this way was notably free from superposed impurities, only a faint trace of the OH band at λ 3064 being visible on a strongly exposed plate. Lines of tin were entirely absent, but it is interesting to note, in view of the possibility of the bands being due to Sn_2, that the resonance lines of tin at $\lambda\lambda$ 2863·3 and 2840·0 appeared in the absorption spectrum of the same flame as described later. With spectrographs of moderate dispersion the exposures were not unduly long, half an hour being sufficient to obtain a strong plate on the Hilger E 2 quartz spectrograph.

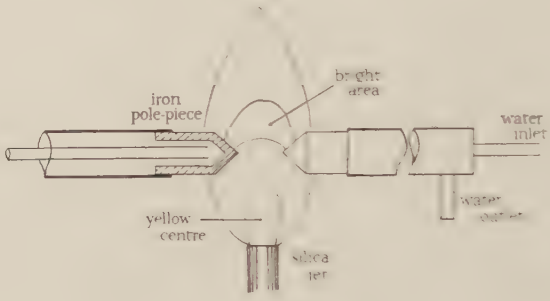


Figure 1.

The source was made very much brighter by passing a high-tension a.-c. arc through the flame, between water-cooled hollow iron pole-pieces about $\frac{1}{2}$ to 1 cm. apart. The arc was fed by a transformer supplying about 0·2 ampere at 5000 volts. The increased luminosity was not confined to the region of the flame directly between the poles, but extended over a crescent-shaped area above them. With this arrangement, figure 1, exposure times were reduced to one-tenth of those required for the flame alone. The spectrum obtained from this arc flame was intermediate between that of the simple flame yielding short bands and that of the metal arc in air giving extended and overlapping bands. A few of the stronger iron lines which appeared in the spectrum could readily be distinguished by means of the iron comparison spectrum. The OH band was rather more strongly developed than

* When titanium chloride, a volatile fuming liquid, was used in place of stannic chloride, a flame of similar form was obtained. There were, however, no signs of titanium-oxide bands. They were either completely masked by the strong continuous spectrum from the white-hot particles of titanium oxide in the central region of the flame, or, as seems more probable, the temperature was not sufficiently high to vaporize or excite the oxide molecules. This view receives confirmation from the work of Dr A. S. King, *Publ. Astr. Soc. Pac.* **36**, 140 (1924), who found that in the electric furnace the TiO bands appeared only at temperatures above 1900° C.

in the normal flame, and as this tended to obscure some of the bands near λ 3200, the flame source was used without the high-tension arc for photographs in this region.

§ 4. THE ABSORPTION SPECTRUM

It became evident, during the consideration of the various electronic levels involved in Mahanti's three systems of bands, that considerable assistance might be expected from an examination of the absorption spectrum. A beam of white light, obtained by burning magnesium ribbon in a holder with a clockwork feed, was passed through a flame of hydrogen containing stannic-chloride vapour as before. In order to give a longer path for absorption, the flame was wide and flat in shape. Metal screens were arranged on either side of the flame to ensure that all the light reaching the slit of the spectrograph had passed through the flame. The magnesium ribbon burnt in this way is a convenient source of continuous radiation in the near ultra-violet region. The absorption spectrum is shown at (*b*) in the plate.

§ 5. THE ACTIVE NITROGEN METHOD OF EXCITATION

The spectra of certain oxides, such as BO and SO, can be conveniently excited by active nitrogen which has not been completely freed from oxygen. Bands produced by active nitrogen are the short bands characteristic of a low-temperature source. Consequently an attempt was made to produce the SnO bands by this means, in order to compare them with those from the flame sources. A quantity of stannic chloride was enclosed in a glass bulb and the vapour was allowed to pass, under control of a tap, into a stream of active nitrogen in the manner adopted by Strutt and Fowler*.

As has been stated by these observers, a bright blue glow is produced where the streams of active nitrogen and tin-chloride vapour come into contact, and the spectrum is characterized by a group of closely spaced narrow bands extending from about λ 4000 to λ 4500. This spectrum is clearly quite different from that given by the flame. No heads can be detected and the contrast between dark and light portions is not very strong, so that it is difficult to observe the bands under large dispersions. Photographs taken on the Hilger E 1 quartz spectrograph do not show any of the structure usually associated with diatomic molecules. This system of bands is therefore apparently not connected with the SnO bands which have been obtained in the flame.

So far as is known these bands have not been investigated further since they were first described by Strutt and Fowler. The similarity in colour between the glow in active nitrogen and the flame makes confusion easy, but the spectra are quite different in character.

* *Proc. R.S.* A, **86**, 105 (1912).

§ 6. DETERMINATION OF WAVE-LENGTHS

Numerous photographs of the flame and high-tension arc in flame were obtained with Hilger E 1, E 2 and small quartz spectrographs, and in the first order of the 10-ft. concave grating of this laboratory. Measurements were made on several of the plates taken with the E 1, E 2 and grating instruments. The dispersions given by these instruments were as follows:

E 2 47 Å./mm. at λ 4300 to 18 Å./mm. at λ 3100,
E 1 16 Å./mm. at λ 4400 to 5 Å./mm. at λ 3100,

10-ft. concave grating 5·4 Å./mm. in the first order.

The larger dispersion on the grating plates did not always give correspondingly greater accuracy in the wave-length measurements of the bands, owing to the rather indefinite nature of the unresolved band lines forming the heads. To obtain the fine structure necessary for the determination of the origins of the bands, which are of greater importance than the heads from a theoretical point of view, would require much higher resolving-power than was available.

Panchromatic plates were used to explore the yellow and red parts of the spectrum, but as no bands were found there, Imperial Ordinary plates were used for the blue and ultra-violet. Measurements were made in the usual way with a Hilger photomicrometer, and the iron lines adopted as standards were, as far as possible, those recommended as secondary standards by the International Astronomical Union.

Particulars of the observed bands are included in table 1, which indicates wave-lengths in air, wave-numbers *in vacuo* and relative intensities of the band heads.

§ 7. VIBRATIONAL ANALYSIS

Mahanti classified the bands he observed into *A*, *B* and *C* systems. Most of the bands have been placed in the *A* system, the other systems being composed of fainter bands towards the less refrangible end.

Table 1 contains, in addition to the measurements, the values of v' and v'' assigned by the author in the empirical analysis of the vibrational structure. It also includes all the bands recorded by Mahanti and shows the system—*A*, *B* or *C*—in which each band was placed by him. It will be seen that during the present investigation a considerable number of bands have been observed which were not included in Mahanti's tables. When a band has been observed by Mahanti, but not found by the author, Mahanti's value of the wave-number is given in square brackets.

The principal bands of the spectrum, and numerous fainter ones, can be arranged in a Deslandres scheme as shown in table 2, v' taking values from 0 to 8 and v'' from 0 to 9.

The bands analysed by Mahanti are those having values of v' from 0 to 3 only. By means of the flame source previously described, the higher members of the v'

Table 1

λ (in air) and intensity	ν (in vacuo)	v', v''	Mahanti's classification	λ (in air) and intensity	ν (in vacuo)	v', v''	Mahanti's classification
4660·9 (1)	21448			3864·87 (3)	25866·8	(2, 6)	
4633·5 (1)	21576			3854·17 (0)	25938·6		*B* (1, 0)
4612·4 (0)	21675			3833·24 (2)	26080·2	(1, 5)	*A* (1, 5)
4590·8 (0)	21777			3802·70 (2)	26289·7	(0, 4)	*A* (0, 4)
4569·5 (0)	21878		*C* (0, 3)	3779·34 (1)	26452·1		
4540·9 (0)	22016			3752·30 (1)	26642·8	(2, 5)	*A* (2, 5)
4522·4 (0)	22106			3721·23 (3)	26865·2	(1, 4)	*A* (1, 4)
4498·7 (1)	22222			3691·39 (5)	27082·4	(0, 3)	*A* (0, 3)
4487·9 (0)	22276		*A* (1, 10)	3677·68 (0)	27183·3	(3, 5)	*A* (3, 5)
4452·48 (1)	22453·1		*C* (1, 3)	3644·6 (0)	27430	(2, 4)	*A* (2, 4)
4428·90 (2)	22572·6			3614·75 (3)	27656·6	(1, 3)	*A* (1, 3)
4411·40 (3)	22662·2		*C* (0, 2)	3585·40 (7)	27883·0	(0, 2)	*A* (0, 2)
4388·47 (0)	22780·6			3574·53 (0)	27967·7	(3, 4)	*A* (3, 4)
	[22831·4]		*A* (2, 10)	3542·39 (1)	28221·5	(2, 3)	*A* (2, 3)
4365·36 (0)	22901·2		*B* (0, 3)	3530·02 (0)	28320·4		
	[23020·0]		*A* (1, 9), *C* (2, 3)	3512·9 (1)	28458	(1, 2)	*A* (1, 2)
				3484·50 (8)	28690·3	(0, 1)	*A* (0, 1)
4302·87 (3)	23233·8		*C* (1, 2)	3475·87 (0)	28761·6	(3, 3)	*A* (3, 3)
	[23194·7]		*A* (0, 8)	3469·16 (0)	28817·2		
	[23380·7]		*A* (3, 10)	3444·64 (3)	29022·3	(2, 2)	*A* (2, 2)
4262·30 (3)	23454·9		*C* (0, 1)	3415·84 (5)	29267·0	(1, 1)	*A* (1, 1)
4240·34 (2)	23576·4	(2, 9)	*A* (2, 9)	3406·94 (1)	29343·5	(4, 3)	
4217·74 (3)	23702·7		*B* (0, 2)	3388·26 (6)	29505·2	(0, 0)	*A* (0, 0)
4174·42 (0)	23948·7		*A* (0, 7)	3381·72 (2)	29562·3	(3, 2)	*A* (3, 2)
4161·00 (1)	24025·9		*C* (1, 1)	3374·66 (1)	29624·1	(6, 4)	
4144·41 (1)	24122·1	(3, 9)	*A* (3, 9), *B* (2, 3)	3351·4 (2)	29830	(2, 1)	*A* (2, 1)
				3344·71 (1)	29889·4	(5, 3)	
4121·61 (2)	24255·5		*C* (0, 0)	3323·45 (7)	30080·6	(1, 0)	*A* (1, 0)
4112·24 (2)	24310·7		*B* (1, 2)	3316·80 (1)	30140·9	(7, 4)	
4108·88 (2)	24330·7	(2, 8)	*A* (2, 8)	3316·22 (1)	30146·1	(4, 2)	
4079·14 (3)	24508·1		*B* (0, 1)	3291·80 (2)	30369·8	(3, 1)	*A* (3, 1)
4068·2 (1)	24574			3286·26 (1)	30421·0	(6, 3)	
4052·2 (1)	24671			3262·37 (6)	30643·8	(2, 0), (8, 4)	*A* (2, 0)
4025·83 (0)	24832·6		*C* (1, 0)				
4019·35 (2)	24872·6	(3, 8)	*A* (3, 8)	3257·64 (1)	30688·2	(5, 2)	
3983·91 (3)	25093·9	(2, 7)	*A* (2, 7)	3229·76 (2)	30953·1	(4, 1)	
3978·72 (2)	25126·6		*B* (1, 1)	3205·79 (4)	31184·6	(3, 0)	*A* (3, 0)
3950·97 (2)	25303·1	(1, 6)	*A* (1, 6)	3202·04 (2)	31221·1	(6, 2)	
3947·58 (1)	25324·8		*B* (0, 0)	3174·44 (1)	31492·5	(5, 1)	
3935·84 (1)	25400·3		*C* (2, 0)	3149·16 (1)	31738·3	(7, 2)	
3919·51 (1)	25506·2	(0, 5)	*A* (0, 5)	3146·74 (2)	31769·6	(4, 0)	
3899·31 (2)	25638·3	(3, 7)	*A* (3, 7)	3121·55 (1)	32026·1	(6, 1)	
	[25737·9]		*B* (2, 1)	3094·41 (0)	32307·0	(5, 0)	
3877·55 (0)	25782·2			3071·86 (0)	32544·1	(7, 1)	

progressions when v'' is constant can readily be seen; in fact the intensities of these progressions are comparable with those of the v'' progressions when v' is constant.

The addition of these bands, together with the estimated photographic intensities, enables the form of the Condon parabola to be examined. It will be seen

Table 2

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	29505·2	28690·3	27883·0	27082·4	26289·7	25506·2				
	575·4	*576·7*	*575*	*574·2*	*575·5*	*574·0*				
1	30080·6	29267·0	(28458)	27656·6	26865·2	26080·2	25303·1			
	563·2	*563*	*564*	*564·9*	*565*	*562·6*	*563·7*			
2	30643·8	(29830)	29022·3	28221·5	(27430)	26642·8	25866·8	25093·9	24330·7	23576·4
	540·8	*540*	*540·0*	*540·1*	*537·7*	*540·5*	*544·4*	*541·9*	*545·7*	
3	31184·6	30369·8	29562·3	28761·6	27967·7	27183·3		25638·3	24872·6	24122·1
	585·0	*583·3*	*583·8*	*581·9*						
4	31769·6	30953·1	30146·1	29343·5						
	537·4	*537·4*	*542·1*	*545·9*						
5	32307·0	31492·5	30688·2	29889·4						
		533·6	*532·9*	*531·6*						
6		32026·1	31221·1	30421·0	29624·1					
		518·0	*517·2*		*516·8*					
7		32544·1	31738·3		30140·9					
					502·9					
8					30643·8					

Brackets ( ) denote that the measurement is only approximate owing to overlapping bands.

from figure 2 that the parabola is of the wide type similar to those shown by the fourth positive bands of CO and the ultra-violet bands of SiO, which are oxides of the elements of the same group of the periodic table as tin.

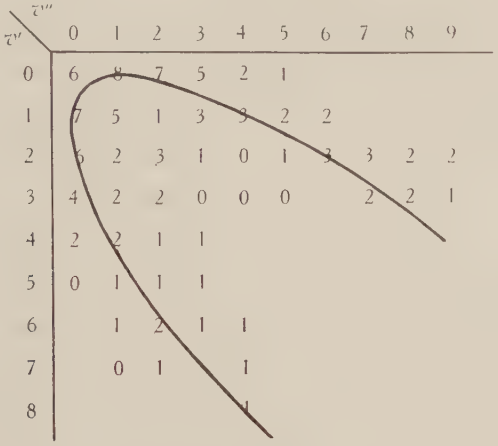


Figure 2. Intensities of bands.

The equation for the origins of the bands of a system is

$$\nu = \nu_e + [\omega_e'(v' + \tfrac{1}{2}) - x_e'\omega_e'(v' + \tfrac{1}{2})^2 + y_e'\omega_e'(v' + \tfrac{1}{2})^3 \ldots] - [\omega_e''(v'' + \tfrac{1}{2}) - x_e''\omega_e''(v'' + \tfrac{1}{2})^2 + y_e''\omega_e''(v'' + \tfrac{1}{2})^3 \ldots],$$

where ω_e is the frequency of vibrations of the nuclei of infinitesimal amplitude;

$x_e, y_e, \ldots$ are small constants taking into account the fact that the vibrations are not quite harmonic;

v is the vibrational quantum number, taking successive integral values 0, 1, 2, 3, ...; and

the superscripts $'$ and $''$ refer to the upper and lower electronic states in accordance with the usual convention.

The resolving power available was not sufficient to obtain data for the band origins, but a similar equation applies to the heads, if slightly different coefficients are used. There is also a term in $(v' + \frac{1}{2})(v'' + \frac{1}{2})$. This is usually small and it could not be determined for these bands. For the SnO band system under consideration the equation derived for the R heads is

$$\nu = 29626{\cdot}1 + [578{\cdot}9(v' + \tfrac{1}{2}) - 1{\cdot}1(v' + \tfrac{1}{2})^2 - 0{\cdot}32(v' + \tfrac{1}{2})^3] - [821{\cdot}9(v'' + \tfrac{1}{2}) - 3{\cdot}6(v'' + \tfrac{1}{2})^2].$$

It will be seen that a term in $(v' + \frac{1}{2})^3$ is required to express the vibrational levels of the upper state, whilst the coefficient y_e'' of $(v'' + \frac{1}{2})^3$ in the lower state is too small to be determined from the data obtained. There also appears to be a perturbation of the level $v'' = 3$, and this discontinuity is not taken into account by the above formula.

There is no indication that other branches form heads. This fact, together with the further fact that the ground states of several of the other oxides of this group of

the periodic table (for instance CO*, SiO† and PbO‡) are all $^1\Sigma$ states, suggests that the ground state of the SnO molecule is also a $^1\Sigma$ state. The reason for considering that the lower state of this A system is the ground state will be seen from the absorption spectrum.

The perturbation of the vibrational level ($v' = 3$) indicated by the Δv values in table 2 is more clearly exhibited in figure 3, in which the wave-number differences between the bands in successive horizontal rows have been plotted.

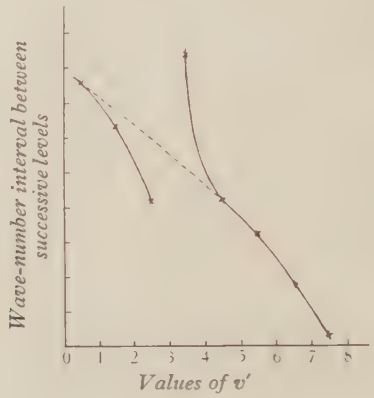


Figure 3.

It will be seen that the intervals between the bands associated with the levels 2 and 3 are smaller than would be expected, whilst the interval between the levels 3 and 4 is much larger than succeeding intervals. After the disturbance has been passed the intervals return to the regular curve, shown dotted near the perturbed level. W. Jevons§ has suggested that some of the so-called vibrational perturbations are actually due to a perturbation of one of the rotational levels, after which the later lines forming the band do not return to their regular positions. If the line structure is not resolved, measurement of the head would make it appear that the whole band was displaced. This may well be the cause of the apparent displacement of the level in the present case, but until the fine structure has been examined the question cannot be decided.

§ 8. ENERGY OF DISSOCIATION

Although it is not possible to follow the v'' progressions as far as the convergence point, an approximate value of the energy required to dissociate the nuclei when in the lower electronic state can be obtained by the extrapolation method of R. T. Birge and H. Sponer‖. This method assumes that the relation between $\Delta G(v)$

* C. P. Snow and E. K. Rideal, *Proc. R.S.* A, **125**, 462 (1929).
† P. G. Saper, *Phys. Rev.* **40**, 465 (1932).
‡ A. Christy and S. Bloomenthal, *Phys. Rev.* **35**, 46 (1930).
§ *Report on Band Spectra of Diatomic Molecules*, p. 203 (Phys. Soc. 1933).
‖ *Phys. Rev.* **28**, 259 (1926).

and v is linear. Within the degree of accuracy obtainable from the experimental data such an assumption is justifiable in this particular case. Examination of the equation giving the positions of the band heads shows that the interval between successive vibrational levels gradually decreases with increasing values of v until, at a certain value of v called $v_{\max.}$, the interval vanishes.

$$v_{\max.} = \omega_e/2x_e\omega_e - \tfrac{1}{2}.$$

This corresponds to the dissociation of the particular state, and by substituting the value of $v_{\max.}$ in the vibrational energy term

$$G(v) = \omega_e(v+\tfrac{1}{2}) - x_e\omega_e(v+\tfrac{1}{2})^2 \qquad G$$

we obtain the value of D_e, the energy of dissociation from the equilibrium position. D_e
The actual energy of dissociation D is less than D_e by the energy of the lowest vibrational level, $v = 0$. D

Hence
$$\begin{aligned} D &= G(v_{\max.}) - G(0) \\ &= \omega_e^2/4x_e\omega_e - \tfrac{1}{2}\omega_e + \tfrac{1}{4}x_e\omega_e \\ &= \tfrac{1}{2}v_{\max.}(\omega_e - x_e\omega_e). \end{aligned}$$

The value of the energy of dissociation D'' in the lower electronic state is thus given by D''

$$\begin{aligned} D'' &= \tfrac{1}{2} \times 113{\cdot}6 \times 818{\cdot}3 \text{ cm.}^{-1} \\ &= 5{\cdot}7 \text{ volts}. \end{aligned}$$

Owing to the apparent perturbation of the level $v' = 3$, the vibrational constants of the upper state cannot be determined with sufficient accuracy to determine the energy of dissociation D' of this state by extrapolation.

§ 9. MAHANTI'S *B* AND *C* SYSTEMS

The formulae given by Mahanti for the band heads in his three systems are as follows:

For the A system

$$\begin{aligned} \nu = 29630{\cdot}5 &+ [586{\cdot}0(v'+\tfrac{1}{2}) - 6{\cdot}0(v'+\tfrac{1}{2})^2] \\ &- [824{\cdot}0(v''+\tfrac{1}{2}) - 4{\cdot}0(v''+\tfrac{1}{2})^2]. \end{aligned}$$

For the B system

$$\begin{aligned} \nu = 25418{\cdot}6 &+ [637{\cdot}0(v'+\tfrac{1}{2}) - 8{\cdot}0(v'+\tfrac{1}{2})^2] \\ &- [824{\cdot}0(v''+\tfrac{1}{2}) - 4{\cdot}0(v''+\tfrac{1}{2})^2]. \end{aligned}$$

For the C system

$$\begin{aligned} \nu = 24370{\cdot}4 &+ [582{\cdot}0(v'+\tfrac{1}{2}) - 4{\cdot}0(v'+\tfrac{1}{2})^2] \\ &- [813{\cdot}5(v''+\tfrac{1}{2}) - 5{\cdot}5(v''+\tfrac{1}{2})^2]. \end{aligned}$$

Since the values of ω_e and $x_e\omega_e$ shown above are the same for the lower levels of the A and the B systems, these transitions should evidently have the same final electronic state. The constants of both the levels of the C system are slightly different from those associated with any of the electronic levels so far considered.

The transitions according to Mahanti are those shown on the left of figure 4. For comparison, the author's suggested scheme is shown on the right.

There was no spectroscopic evidence to show which of the levels a or X was the lower, but by comparing the value of the energy of dissociation, deduced from extrapolation of the vibrational levels of the lower electronic state of the C system, with the thermochemical value, Mahanti decided that the level X was the ground state. Such extrapolations are, however, only approximate, even when accurate data are available, so that in the present instance, where there are only a small number of bands in the system, the value of the energy of dissociation may be considerably in error.

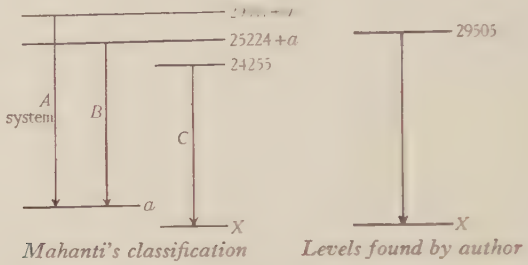


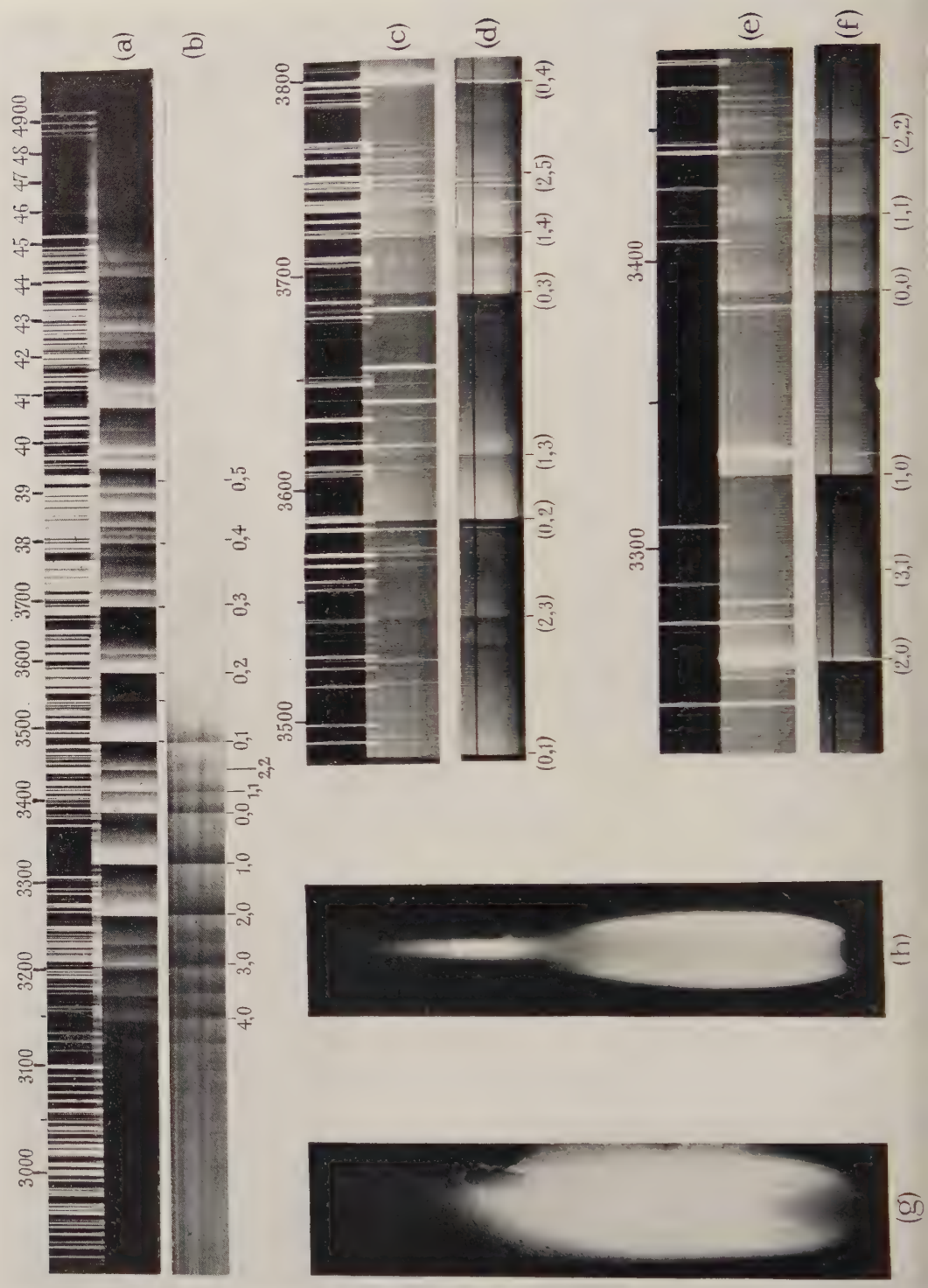
Figure 4.

Examination of the absorption spectrum, shown at (*b*) in the plate, showed that only bands of the A system appeared. Owing to the relatively high temperature at which absorption was occurring, not only was the v' progression (0, 0), (1, 0), (2, 0), ... visible, but also the (0, 1), (1, 1), (2, 1), ..., which appeared with much lower intensity. This is, of course, to be expected, since there is probably an appreciable concentration of SnO molecules in the states $v'' = 1$ or even 2, at the temperature of the hydrogen flame. The temperature could be reduced by mixing nitrogen with the hydrogen supplied to the burner. But the reduced intensity of the flame prevented any great use of this method from being made.

There was no sign of the B system in the absorption spectrum, although this, according to Mahanti, has the same final level and is actually a more probable transition, since less energy would be required than for the production of the A system.

The presence of the A system alone in absorption suggests that the lower electronic state in this system must be the ground state of the molecule. In spite of the similarity in some of the vibrational constants, the final level of the so-called B system cannot also be the ground state. The actual existence of the principal bands in the B and C systems has been confirmed, but it is very doubtful, in view of the small number of bands in each system, their weak intensities, and the evidence given by absorption, whether these bands really do form parts of separate systems. At the same time it must be admitted that it has not been found possible to incorporate the bands concerned into the principal A system.

The possibility of the upper electronic level being triple has also been con-


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
3000
3100
3200
3300
3400
3500
3600
3700
3800
3900
4000
4100
4200
4300
4400
4500
4600
4700
4800
4900
4,0
3,0
2,0
1,0
0,0
1,1
2,2
0,1
0,2
0,3
0,4
0,5
(0,1)
(2,3)
(0,2)
(1,3)
(0,3)
(1,4)
(2,5)
(0,4)
(2,0)
(3,1)
(1,0)
(0,0)
(1,1)
(2,2)

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sidered, but no satisfactory arrangement has been found. It is also possible that the spectrum is due to a polyatomic oxide molecule. In addition to these bands of Mahanti's *B* and *C* systems, there are a number of other bands which remain unclassified. These were not recorded by Mahanti.

§ 10. ACKNOWLEDGMENT

The author wishes to express sincere thanks to Prof. A. Fowler, F.R.S., for valuable advice during the work, and to Dr W. Jevons and Dr R. W. B. Pearse for many helpful suggestions.

DESCRIPTION OF PLATE

(*a*) General view of spectrum of SnO in flame source, with the Hilger E 2 quartz spectrograph. To avoid confusion only the principal bands are marked.

(*b*) Absorption spectrum on same scale as (*a*), showing v' progressions ($v'' = 0$ and 1).

(*c*) and (*e*) Parts of spectrum of metallic arc in air under higher dispersion, with the Hilger E 1 quartz Littrow.

(*d*) and (*f*) Spectrum obtained from high-tension arc in flame. Bands are intermediate in character between flame (*a*) and arc (*c*) and (*e*). Note comparative freedom from interference by extraneous spectra.

(*g*) Flame of hydrogen containing stannic-chloride vapour. The inner region is yellow, the outer mantle bright blue.

(*h*) Similar flame to (*g*), but with nitrogen mixed with hydrogen. The yellow region is now above rest of flame.

550.83 : 519.281.2

THE RAPID ADJUSTMENT OF OBSERVATIONS IN A NETWORK OF GEOPHYSICAL STATIONS BY THE METHOD OF LEAST SQUARES

By E. LANCASTER JONES, B.A.

Communicated by Prof. A. O. Rankine, July 28, 1933

ABSTRACT. A frequent problem in geodesy and geophysics concerns the adjustment of a set of values for a physical magnitude at a number of stations. The values are obtained from other observed magnitudes by computations involving the geometrical links of the station network, and there is ambiguity on account of the multiplicity of connections. Since the magnitude desired is single-valued at each station, the values obtained are usually adjusted by the method of least squares. Where the number of stations is large and the network is complex, the normal equations for least-square adjustment are very numerous and their solution by standard procedure is tedious. The paper develops a method of establishing the normal equations, and solving them by successive approximations, which is simple, rapid and satisfactory in practice, and is applicable to any network, however large and complex. Although particular attention is focused on the problem of obtaining isogams from observations of gravity gradients in applied geophysics, the method has obvious applications in other fields where the mathematical conditions are similar.

§ 1. INTRODUCTION

In many branches of geodesy and geophysics, observations of physical magnitudes are made at a series of stations which form a network of triangles or polygons. From these measured magnitudes it is frequently desired to compute the values of other magnitudes at the stations concerned. By reason of the relationship between the observed and computed magnitudes, and the geometry of the network, it usually happens that there is ambiguity in the final values attained, and it is customary to apply the method of least squares to resolve the ambiguity.

A particular example occurs in applied geophysics in the computation of isogams from observations of the gradients of gravity at stations of the network. The difference in gravity $g_B - g_A$ at two stations A, B of the network may be obtained by taking any path formed of straight lines joining adjacent stations between A and B, assuming that the average gradient of gravity along the rectilinear sections of the path is equal to the mean of the values at the two stations connected by it, and taking the sum of the sectional differences of gravity thus computed. Thus, if P and Q are any two consecutive stations on the path chosen, and if their co-ordinates are (x_1, y_1) and (x_2, y_2) whilst their component gravity-gradients are (X_1, Y_1) and (X_2, Y_2) respectively, we have

$$2\,(g_B - g_A) = \Sigma_A^B\,[(X_1 + X_2)\,(x_2 - x_1) + (Y_1 + Y_2)\,(y_2 - y_1)].$$

If, however, we take another path connecting A to B and involving other intervening stations, we shall usually obtain a different value for $g_B - g_A$.

This is a particular case of a more general problem concerned with single-valued functions, and it is with this general class that we are concerned.

§ 2. THE PROBLEM

Given a network of stations $A, B, C, \ldots$ and the observed or computed values of the increments (ab), (bc), $(ca), \ldots$ between adjacent stations of a single-valued function U, we have to find the best possible values of U at $A, B, C, \ldots$. $(ab),(bc),(ca)$ U

The problem resolves itself into one which may be expressed thus: To find the adjusted values (AB), (BC), $(CA), \ldots$ of the increments (ab), (bc), $(ca), \ldots$, respectively, where, around any closed polygonal path $ABC \ldots PA$, we have the condition that $(AB), (BC), (CA)$

$$(AB) + (BC) + (CD) + \ldots + (PA) = 0,$$

whereas, in general

$$(ab) + (bc) + (cd) + \ldots + (pa) \neq 0 \text{ but} = \text{some value } d. \qquad d$$

We may call d the "excess" around the path $ABC \ldots PA$.

In the particular cases of gravitational and magnetic observations in applied geophysics, this problem and its solution by the method of least squares have been considered by I. Roman*. Roman states the problem in a different but equivalent manner and obtains rather more complex normal equations, which he solves by the usual reduction method of Gauss.

The present writer believes that the treatment given below is particularly adapted to this problem. The normal equations are simple and can be written down by inspection. Methods of resolution of these equations are suggested which are much less laborious than the Gaussian reduction methods, and permit the labour of reduction to be accommodated to the particular degree of accuracy in adjustment which is considered worth while. Most practical geophysicists are agreed that an elaborate, ultra-precise least-square adjustment of their observations is an unwarranted expenditure of time and labour. On the other hand, some adjustment is obviously necessary.

§ 3. THE NORMAL EQUATIONS

In the terms used in treatises on the method of least squares†, we have given a series of "conditional" equations

$$(AB) = (ab),$$
$$(BC) = (bc),$$
$$(CA) = (ca),$$
$$\ldots\ldots\ldots\ldots$$

* *Trans. Amer. Inst. Min. Metall. Engrs.* "Geophysical Prospecting", 460 (1932).

† Whittaker, E. T. and Robinson, G., *The Calculus of Observations*, chap. IX, and particularly § 129, pp. 252–254 (1924).

together with a series of "rigorous" equations

$$(AB) + (BC) + (CA) = 0,$$

.....

There is one conditional equation for every link in the network, and one rigorous equation for every *independent* polygon in the network. We shall assume that all the observations and link-increments such as (ab) have equal weight.

For such a system of conditional and rigorous equations, the normal equations for a least-square adjustment are obtained as follows. For each rigorous equation, provide an unknown multiplier or correlate m. The unknown increment (PQ), which occurs in one only of the conditional equations, namely $(PQ) - (pq) = 0$, occurs also in at most two of the rigorous equations. For normally it will be a common section of the boundary of two adjacent polygons, e.g. $OPQR$, $SQPT$, figure 1, and at the extreme boundaries of the network one of these polygons will be absent. The increments (pq), (PQ) are of course algebraical quantities, so that $(pq) = -(qp)$, $(PQ) = -(QP)$.

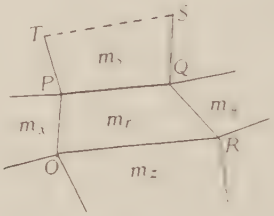

Figure 1.

If we assume that the polygonal circuits such as $OPQR$ are always traversed in the same direction, e.g. clockwise, then (PQ) occurs positively in $OPQR$, but negatively in $SQPT$.

For such a link as (PQ) there will result a normal equation

$$(PQ) = (pq) - m_r + m_s \qquad \text{.....(1)},$$

m_r, m_s where m_r and m_s are the multiplier correlates attached to the polygons $OPQR$ and $SQPT$ respectively.

Similarly for every other link, except on the boundary of the network where one of the m's will be absent.

Since the rigorous equations continue to be satisfied, we can replace every term such as (PQ) in them by its equivalent in the above equation. We thus get a series of equations, one for each independent polygon, of the form (see figure 1).

$$(op) - m_r + m_x + (pq) - m_r + m_s + (qr) - m_r + m_y + (ro) - m_r + m_z = 0,$$

where the polygons x, y and z as well as s also touch polygon r at OP, QR and RO respectively.

Thus, for a four-sided polygon r, having contacts with four others x, s, y and z, we have an equation

$$4m_r - m_x - m_s - m_y - m_z = (op) + (pq) + (qr) + (ro)$$
$$= d_r,$$

where d_r is the observed or computed excess around the polygon. Similarly, for an n_r-sided polygon r, which has contacts with adjacent polygons x, s, y, ... , we have an equation

d_r n_r

$$n_r m_r - m_x - m_s - m_y - \ldots = d_r \qquad \ldots\ldots(2).$$

There is one such equation for each independent polygon of the network, so that, for the set of unknown multipliers or correlates m, we have an equal number of linear equations such as (2). From these we can obtain uniquely each of the correlates m_1, m_2, ... , and by using equations (1) we can then obtain quite simply each adjusted link increment (PQ). The whole procedure thus hinges on the solution of the set of correlate equations (2). As has been stated and demonstrated above, these can be written down for any network by inspection.

§ 4. SOLUTION OF THE CORRELATE EQUATIONS. APPROXIMATIONS

The series of correlate equations of the type

$$n_r m_r - \Sigma m_x = d_r$$

can be solved by any of the methods appropriate to linear equations, including that of Gauss. This series is, however, obviously adapted to solution by gradual approximation. Every coefficient is unity except those for the key correlates such as m_r, and these are integers not less than 3.

As a first approximation, we can put

$$m_r = m_r' + \Delta m_r,$$

where $m_r' = d_r/n_r$. m_r'

Similarly

$$m_x' = d_x/n_x \qquad \ldots\ldots(3),$$
$$m_y' = d_y/n_y,$$
$$\ldots\ldots\ldots\ldots$$

whence

$$\Delta m_r = \frac{1}{n_r}\Sigma m_x = \frac{1}{n_r}\Sigma d_x/n_x + \frac{1}{n_r}\Sigma \Delta m_x.$$

Writing

$$m_r'' = \frac{1}{n_r}\Sigma d_x/n_x \qquad \ldots\ldots(4), \qquad m_r''$$

we have $m_r' + m_r''$ as a second approximation to m_r.

Similarly we can find the values m_x'', m_s'', ... and obtain a third approximation $m_r' + m_r'' + m_r'''$ to m_r by writing

$$m_r''' = \frac{1}{n_r}\Sigma m_x'' \qquad \ldots\ldots(5). \qquad m_r'''$$

The procedure can be continued as far as desired, and can be terminated at any stage when the added increments to m_r', m_r'', m_r''', ... become sufficiently small. It is simple and lends itself to routine execution.

Although exact solutions for particular networks, and methods of more rapid approximation, will be discussed later, we may test this particular method for the case discussed by Roman in the paper previously cited.

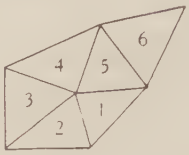

Figure 2.

Figure 2 illustrates the network solved by Roman. There are seven station points and six triangles. In table 1, column d gives the original excesses for each triangle. The successive approximations to the m's are calculated from these d's and the previously obtained approximations for the adjacent triangles given in the third column.

Table 1

Δ	d	Adjacent Δs	m'	$3m''$	m''	$3m'''$	m'''	$3m^{iv}$	m^{iv} ...
1	+ 5	2 + 5	1·667	5	1·667	− 3·333	− 1·111	0·741	0·247 ...
2	+ 10	1 + 3	3·333	− 1·666	− 0·556	0·556	0·185	− 1·481	− 0·494 ...
3	− 10	2 + 4	− 3·333	− 3·334	− 1·111	− 0·110	− 0·370	− 1·111	− 0·370 ...
4	− 20	3 + 5	− 6·667	− 1·666	− 0·556	− 3·889	− 1·296	0·186	0·062 ...
5	+ 5	1 + 4 + 6	1·667	− 8·333	− 2·778	1·667	0·556	− 3·333	− 1·111 ...
6	− 10	5	− 3·333	1·667	0·556	− 2·778	− 0·926	0·556	0·185 ...

The residuals do not disappear very rapidly, but the procedure is easy and rapid.

The values for m obtained by summing the first four elements m' to m^{iv} are within 1·0 of the correct values, and would be quite near enough in practice for obtaining the values of gravity at the stations and drawing up the isogam chart. The original link-increments from which the d's were calculated were of the order of 50 units, so that the final values adjusted on the basis of this fourth approximation would be correct within 2 per cent, which is the limit for gravity work of this type. The final values, obtained by putting m equal to $m' + m'' + m''' + m^{iv}$ are $m_1 = 2{\cdot}47$, $m_2 = 2{\cdot}47$, $m_3 = -5{\cdot}19$, $m_4 = -8{\cdot}46$, $m_5 = -1{\cdot}67$, $m_6 = -3{\cdot}52$, which should be compared with the values obtained in the next section.

A more rapid approximation in the solution of the set of correlate equations

$$n_r m_r - \Sigma m_x = d_r$$

can be obtained by solving partially for those which involve m_r, as follows.

We have, say,

$$n_r m_r - m_x - m_s - m_y - m_z = d_r,$$
$$n_x m_x - m_r - m_a - m_b - \ldots = d_x,$$
$$n_s m_s - m_r - m_e - m_f - \ldots = d_s,$$
$$n_y m_y - m_r - m_h - m_k - \ldots = d_y,$$
$$n_z m_z - m_r - m_p - m_q - \ldots = d_z.$$

From which we can obtain, by dividing the second by n_x, third by n_s, ... and adding

$$m_r\left(n_r - \Sigma\frac{1}{n_x}\right) - \Sigma\frac{1}{n_x}(m_a + m_b + \ldots) = d_r + \Sigma\frac{d_x}{n_x}.$$

For a first approximation m_r' we can put

$$m_r' = \left(d_r + \Sigma\frac{d_x}{n_x}\right)\Big/\left(n_r - \Sigma\frac{1}{n_x}\right) \qquad \ldots\ldots(6),$$

and subsequent increments to this are given by

$$m_r'' = \left(\Sigma\frac{1}{n_x}(m_a' + m_b' + \ldots)\right)\Big/\left(n_r - \Sigma\frac{1}{n_x}\right) \qquad \ldots\ldots(7),$$

$$m_r''' = \left(\Sigma\frac{1}{n_x}(m_a'' + m_b'' + \ldots)\right)\Big/\left(n_r - \Sigma\frac{1}{n_x}\right) \qquad \ldots\ldots(8),$$

.....

When all the polygons concerned have the same number n of sides, the formulae become

$$m_r' = (nd_r + \Sigma d_x)/(n^2 - n_r') \qquad \ldots\ldots(9),$$

where n_r' is the number of polygons adjacent to, or at "first remove" from, the key polygon r.

Also

$$\left.\begin{aligned} m_r'' &= \Sigma m_a'/(n^2 - n_r') \\ m_r''' &= \Sigma m_a''/(n^2 - n_r') \\ &\ldots\ldots\ldots \end{aligned}\right\} \qquad \ldots\ldots(10),$$

Here Σ denotes the series of polygons excluding r which are at second remove from r, i.e. are adjacent to these at first remove from r.

We can again illustrate this system of approximation with reference to the network of six triangles previously considered, figure 2. Table 2 defines the constants concerned in each triangle, n being equal to 3 throughout.

Table 2

Δ	d	1st-remove Δs	2nd-remove Δs	$n^2 - n_r'$	$nd_r + \Sigma d_x$
1	+ 5	2, 5	3, 4, 6	7	30
2	+ 10	1, 3	4, 5	7	25
3	− 10	2, 4	1, 5	7	− 40
4	− 20	3, 5	1, 2, 6	7	− 65
5	+ 5	1, 4, 6	2, 3	6	− 10
6	− 10	5	1, 4	8	− 25

In table 3, where $N_r = n^2 - n_r'$, the approximations are shown worked out to m^{v}, at which stage the residues are well below 0·1 and the values obtained for the m's are within 0·02 of the correct values. This would be an over-elaborate refinement in practice, but illustrates the rapidity of approximation obtainable by the method.

Table 3

N	Δ	m'	Δ''	$+m''-$	$+m'''-$	$+m^{iv}-$	$+m^{v}-$	m
7	1		3	5·714	0·374	0·421	0·020	4·347
			4	9·286	0·676	0·683	0·019	− 2·798
			6	3·125	0·625	0·239	0·078	
				18·125	0·425	1·343	0·117	
		4·286	m	− 2·589	0·061	− 0·192	− 0·017	1·549
7	2		4	9·286	0·676	0·683	0·019	3·617
			5	1·667	0·357	0·199	0·063	− 1·703
				10·953	0·319	0·882	0·082	
		3·571	m	− 1·565	0·046	− 0·126	− 0·012	1·914
7	3		1	4·286	2·589	0·061	0·192	0·374
			5	1·667	0·357	0·199	0·063	− 6·191
				2·619	2·946	0·138	0·255	
		− 5·714	m	0·374	−0·421	− 0·020	− 0·036	− 5·817
7	4		1	4·286	2·589	0·061	0·192	
			2	3·571	1·565	0·046	0·126	0·676
			6	3·125	0·625	0·239	0·078	− 10·045
				4·732	4·779	0·132	0·396	
		− 9·286	m	0·676	− 0·683	− 0·019	− 0·059	− 9·369
6	5		2	3·571	1·565	0·046	0·126	
			3	5·714	0·374	0·421	0·020	
				2·143	1·191	0·375	0·146	
		− 1·667	m	− 0·357	− 0·199	− 0·063	− 0·024	− 2·310
8	6		1	4·286	2·589	0·061	0·192	
			4	9·286	0·676	0·683	0·019	
				5·000	1·913	0·622	0·211	
		− 3·125	m	− 0·625	− 0·239	− 0·078	− 0·026	− 4·093

The final values obtained are

$$m_1 = 1{\cdot}55,\ m_2 = 1{\cdot}91,\ m_3 = -5{\cdot}82,\ m_4 = -9{\cdot}37,\ m_5 = -2{\cdot}31,\ m_6 = -4{\cdot}09.$$

§ 5. RECTANGULAR NETWORKS

The case of a rectangular network has a particular importance, since it corresponds to an ideal arrangement of stations often used in practical geophysical surveys on suitable terrain.

Referring to equations (9) and (10) of § 4, we have

$$n = 4 \text{ and } n_r' = 1, 2, 3 \text{ or } 4 \text{ generally.}$$

$$\therefore\ N_r = n^2 - n_r' = 12, 13, 14 \text{ or } 15,$$

and we can solve by successive approximation, as in the case of triangles, using the formulae

$$\left.\begin{aligned} m_r' &= (4d_r + \Sigma d_a)/N_r \\ m_r'' &= \Sigma m_a'/N_r \\ m_r''' &= \Sigma m_a''/N_r \\ &\cdots\cdots\cdots\cdots \end{aligned}\right\} \quad \ldots\ldots(11),$$

which give approximations approaching the complete solution m_r with rapidity rather greater than in the case of triangles.

It should be carefully noted that, throughout the above reasoning, we have assumed that each first-remove and second-remove polygon is independent. If any polygon occurs as a common second-remove to two first-remove polygons, it must be counted twice in the sums $\Sigma m_a'$, $\Sigma m_a''$, ...

§ 6. SOLUTIONS OF INCREASING PRECISION. RECTANGULAR NETWORKS

In networks which have a regular pattern, whether of triangles or rectangles, formulae can be developed for expressing the correlate of any particular figure (polygon) in terms of the excesses of its surrounding figures, to any degree of remoteness.

Previously we have only considered the elimination of the first-remove polygons, leaving the second-remove ones as first residuals. We next consider how to eliminate polygons of second and greater remoteness.

Figure 3 shows a rectangular network in which the rectangles are numbered from one corner 00 in rows and columns.

00	01	02	03	04
10	11	12	13	14
20	21	22	23	24
30	31	32	33	34

Figure 3.

Any rectangle has a number of first-remove rectangles varying from 2 to 4 according to its position at a corner of the complete network, on the outer run or in the interior of the network.

From the geometry, each first-remove rectangle may have contact with a second-remove rectangle which is common to another first remove. For instance, 11 is common to 01 and 10, both first removes of 00.

We shall first find expressions for the correlate of any rectangle, eliminating both the first-remove and the common second-remove correlates. The corner rectangle 00 has two first removes and one common second remove, and the correlate equations are

$$\begin{aligned} 4m_{00} - m_{01} - m_{10} &= d_{00}, \\ -m_{00} + 4m_{01} - m_{11} - m_{02} &= d_{01}, \\ -m_{00} + 4m_{10} - m_{11} - m_{20} &= d_{10}, \\ -m_{01} - m_{10} + 4m_{11} - m_{12} - m_{21} &= d_{11}. \end{aligned}$$

m_{rs}, d_{rs}

Multiplying the equations by 7, 2, 2 and 1 respectively and adding, we eliminate m_{01}, m_{10} and m_{11} and obtain

$$24m_{00} - 2(m_{02} + m_{20}) - (m_{12} + m_{21}) = 7d_{00} + 2(d_{01} + d_{10}) + d_{11} \quad \ldots\ldots(12),$$
$$= 24D_{00}, \text{ say,}$$

D_{rs}

and $m_{00}' = D_{00}$ gives a good approximation to m_{00}, which can be continued by writing

m_{rs}', m_{rs}'', m_{rs}'''

$$m_{00} = m_{00}' + m_{00}'' + m_{00}''' + \ldots,$$

where
$$24m_{00}'' = 2(m_{02}' + m_{20}') + m_{12}' + m_{21}',$$
$$24m_{00}''' = 2(m_{02}'' + m_{20}'') + m_{12}'' + m_{21}'',$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

and these m_{02}', m_{20}', ... are approximations similarly obtained. The rectangles such as 01, 02, ..., 10, 20, ..., which are on the boundary but not in corners, have each three first-remove and two common second-remove rectangles. Two of the first removes are on the boundary and one is in the interior; this third interior rectangle touches both the common second removes.

For 01, for instance, the correlate equations are expressed as shown in table 4, by means of the coefficients only, all applicable to any one m being in the same column while all applicable to any one rectangle are in the same row as its excess d.

Table 4

d	m_{01}	m_{00}	m_{11}	m_{02}	m_{10}	m_{12}	Residues
01	4	− 1	− 1	− 1			
00	− 1	4			− 1		
11	− 1		4		− 1	− 1	$-m_{21}$
02	− 1			4		− 1	$-m_{03}$
10		− 1	− 1		4		$-m_{20}$
12			− 1	− 1		4	$-m_{13} - m_{22}$

Multiplying by 52, 15, 17, 15, 8 and 8 respectively and adding, we get

$$161m_{01} - 17m_{21} - 15m_{03} - 8(m_{20} + m_{13} + m_{22}) = 161D_{01} \quad \ldots\ldots(13),$$

where
$$161D_{01} = 52d_{01} + 17d_{11} + 15(d_{00} + d_{02}) + 8(d_{10} + d_{12})$$

and $m_{01}' = D_{01}$ gives a first approximation to m_{01}. It should be noted that all the rectangles whose correlates are thus eliminated are those which are laterally and diagonally once-removed from the key rectangle 01, whilst the residual correlates m_{20}, m_{21}, m_{22}, m_{03} and m_{13} are the ones adjacent externally to those eliminated.

Similarly for 02 we should get

$$161m_{02} - 17m_{22} - 15(m_{00} + m_{04}) - 8(m_{10} + m_{21} + m_{23} + m_{14})$$
$$= 52d_{02} + 17d_{12} + 15(d_{01} + d_{03}) + 8(d_{11} + d_{13}),$$

and so on for any other boundary rectangle not a corner.

The drawback to the above series for $m_{01}, m_{02}, \ldots$ is that the coefficients involved are not so simple as in the case of equations (11) and (12). There is some advantage in using for these rectangles the same multipliers, namely 7, 2 and 1 for the key equation, for all first-remove equations and for common second-remove equations, as were used in equation (12).

These give the equation

$$22m_{01} - m_{11} - 2(m_{21} + m_{03}) - (m_{20} + m_{13} + m_{22}) = 7d_{01} + 2(d_{00} + d_{11} + d_{02}) + d_{10} + d_{12} = 22D_{01}' \quad \ldots\ldots(14),$$

in which m_{11} is left as an additional residual to the previous series; but the series of residuals left for m_{01}'', after we have written

$$m_{01} = m_{01}' + m_{01}'' + \ldots \text{ and } m_{01}' = D_{01}',$$

is very easy to use for further approximation.

For the inner rectangles, such as 11, 12, 21, 22, ..., which have four first-remove and four common second-remove rectangles, together forming a rectangle of three by three cells, we use multipliers 6, 2 and 1 respectively for each order of remoteness and obtain

$$\begin{aligned} 20m_{11} - 2(m_{13} + m_{31}) - (m_{03} + m_{23} + m_{32} + m_{30}) &= 6d_{11} + 2(d_{01} + d_{12} + d_{21} + d_{10}) + (d_{00} + d_{02} + d_{22} + d_{20}), \\ 20m_{12} - 2(m_{10} + m_{32} + m_{14}) - (m_{00} + m_{04} + m_{24} + m_{33} + m_{31} + m_{20}) &= 6d_{12} + 2(d_{11} + d_{02} + d_{13} + d_{22}) + (d_{01} + d_{03} + d_{23} + d_{21}), \\ \ldots\ldots\ldots\

cells $S-3$ and $S-3$. We have the correlate equation coefficients shown in table 5.

Table 5

m									d	$\times$ by
$S-4$	$S-3$	$S-2$	$S-1$	S	$S+1$	$S+2$	$S+3$	$S+4$		
			- 1	4	- 1				$= S$	56
		- 1	4	- 1					$= S-1$	15
				- 1	4	- 1			$= S+1$	15
	- 1	4	- 1						$= S-2$	4
					-1	4	- 1		$= S+2$	4
- 1	4	- 1							$= S-3$	1
						- 1	4	- 1	$= S+3$	1

And using the multipliers 1 for $S-3$ and $S+3$, 4 for $S-2$ and $S+2$, $(4\times 4-1)$ or 15 for $S-1$ and $S+1$, and $(4\times 15-4)$ or 56 for S, and adding, we get

$$194m_S - m_{S-4} - m_{S+4} = 56d_S + 15\,(d_{S-1}+d_{S+1}) + 4\,(d_{S-2}+d_{S+2}) + (d_{S-3}+d_{S+3}) \quad \ldots\ldots(16),$$

which gives a very rapid approximation for any central cell S. For cells near and at the ends of the chain the same multipliers are valid, but the residual m's have slightly different coefficients. For example, if the chain terminates in $S-2$, the above equation still holds for m_S if the term $-m_{S-4}$ on the left is replaced by $+m_{S+2}$ and d_{S+3} is omitted on the right.

The series of multipliers available for such a single chain of rectangular cells is the series

$$1, 4, 15, 56, \ldots p_r,$$

p_r where $$p_r = 4p_{r-1} - p_{r-2} \quad \ldots\ldots(17),$$

for any positive integral value of r,

and $$p_1 = 1,\ p_2 = 4.$$

§ 7. TRIANGULAR NETWORKS. MORE RAPID APPROXIMATIONS

As in the case of the rectangular networks just considered, so in triangular networks can more rapid approximations for the correlate of any cell be obtained by eliminating the correlates for second- as well as first-remove triangles.

As the triangles will normally be restricted to those in which no angle is less than 45° and none greater than 90°, we can assume that only rare instances will occur of common second-remove cells. The normal case will be one in which each triangular cell has from one to three first-remove triangles touching it, and each of these has one or two independent second-remove triangles in external contact with it.

Single chain of triangles. Consider the case of figure 5, which relates to triangular cells in the same way that figure 4 relates to rectangular cells.

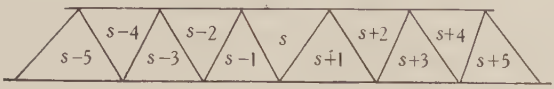

Figure 5.

The table of correlate equations with cell 5 as centre is shown in table 6.

Table 6

m											d
$S-5$	$S-4$	$S-3$	$S-2$	$S-1$	S	$S+1$	$S+2$	$S+3$	$S+4$	$S+5$	
				−1	3	−1					S
			−1	3	−1						$S-1$
					−1	3	−1				$S+1$
		−1	3	−1							$S-2$
						−1	3	−1			$S+2$
	−1	3	−1								$S-3$
							−1	3	−1		$S+3$
−1	3	−1									$S-4$
								−1	3	−1	$S+4$

As before, we can find a series of multipliers, namely

$$1, 3, 8, 21, 55, \ldots p_{r-2}, p_{r-1}, p, \ldots,$$

where

$$p_r = 3p_{r-1} - p_{r-2} \qquad \ldots\ldots(18),$$

$$p_2 = 3,$$

$$p_1 = 1,$$

which will eliminate all the correlates of intermediate pairs of triangles down to any desired residue, e.g. $S \pm 5$. For example, to eliminate from $S \pm 1$ to $S \pm 4$ inclusive, we use the series to the 5th term 55 and get

$$123m_S - m_{S-5} - m_{S+5} = 55d_S + 21\,(d_{S-1} + d_{S+1}) + 8\,(d_{S-2} + d_{S+2}) + 3\,(d_{S-3} + d_{S+3}) + d_{S-4} + d_{S+4} \qquad \ldots\ldots(19).$$

For cells near or at a terminus of the chain, we use the same series of multipliers.

For triangles with two second-remove cells to each first-remove cell we use the multiplier series 1, 3, 7; for instance, in the network of figure 6*a*, cell 0 has one first-remove cell 11 and this has two second-remove cells, 21 and 22.

The correlate table for m_0 is table 7.

Table 7

0	11	21	22	d	p
3	−1			0	7
−1	3	−1	−1	11	3
	−1	−3		21	1
	−1		3	22	1

whence, multiplying (see column p) by 7, 3, 1 and 1 respectively,

$$18m_0 = 7d_0 + 3d_{11} + d_{21} + d_{22} \quad \text{.....(20).}$$

Similarly, in the network of figure 6*b*, we should get

$$12m_0 = 7d_0 + 3\,(d_{11} + d_{12} + d_{13}) + d_{21} + d_{22} + d_{23} + d_{24} + d_{25} + d_{26} \quad \text{.....(21).}$$

n_1 The coefficient of m_0 is always $21 - 3n_1$, where n_1 is the number of first-remove cells.

Figure 6*a*.

If in the network of triangles actually under consideration there are third-remove triangles, or triangles of still greater remoteness from the key triangle for which approximation is desired, there will be residual correlates, $m_{31}, m_{32}, \ldots$, introduced into equations of type (19) and (20). There is no difficulty in finding series of multipliers to carry the elimination to further stages, especially if the cells

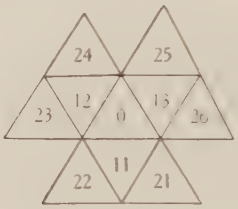

Figure 6*b*.

are arranged symmetrically about the key cell. For example, the network of figure 6*b* may be completed by the insertion of three triangles 31, 32 and 33 between 22 and 23, and 24 and 25, and 26 and 21 respectively, giving three extra common third-remove triangles. The desired series of multipliers is then 2, 3, 7 and 15 and we get

$$24m_0 = 15d_0 + 7\,(d_{11} + d_{12} + d_{13}) + 3\,(d_{21} + \ldots + d_{26}) + 2\,(d_{31} + d_{32} + d_{33}) \quad \text{...(22).}$$

§ 8. GENERAL NETWORK. PROCEDURE FOR ADJUSTMENT

The foregoing analysis will have made quite clear the limitless possibilities of mathematical solution by means of correlate equations and multipliers suited to any cell of a network and its immediate surroundings. Interesting as such analysis is, its application to a practical problem of least-square adjustment must be governed by considerations of the accuracy justified in the particular survey, and the most economical method of executing the calculations involved. Adjustment involving elimination of the correlates of the first-remove cells on the lines of §§ 4 and 5,

using equations (6) to (11), is a simple, reasonably rapid process, readily applicable to any cell in any network however complicated. When the network is homogeneous, i.e. when all the cells are polygons of the same species and regular in arrangement, the more rapid approximations discussed in §§ 6 and 7 may be used with advantage. Also when there are outstanding runs or chains of cells equations (16) to (19) are easy to apply and give very rapid approximations.

For general purposes, the procedure of §§ 4 and 5 is recommended as being simple, universally applicable and almost as rapid as any of the subsequent processes when account is taken of all the stages of the operation. As a test of this procedure, an adjustment made for a network of 56 Eötvös gravity stations may be cited. The observations were made in the course of a practical survey in Cumberland. The stations are shown as open circles in figure 7, where they are connected by broken-

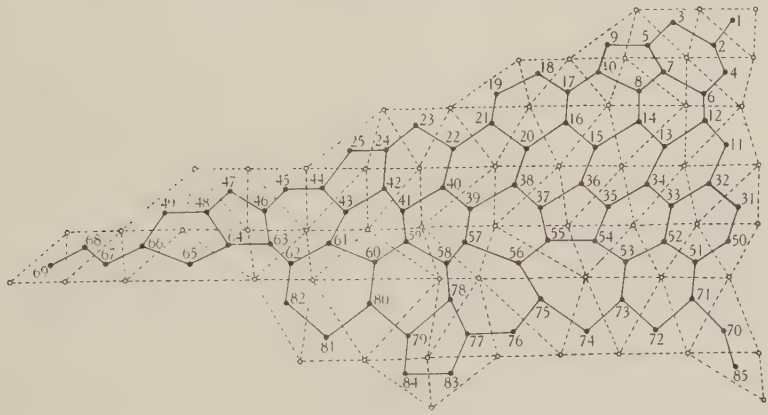

Figure 7.

line links to form 80 triangles numbered 1 to 85, numbers 26 to 30 being omitted. It is evident that the network thus formed is typical of a large regional survey and that the procedure of linking could be adapted to any group of stations, however numerous. From the measured data of the gravity survey the increments in g were calculated for every link, and from these the excesses were derived for each triangle of the network. The excesses for the first ten triangles are tabulated in table 8 in

Table 8

Δ	d'	$\Sigma_1^{iv} m$	d^{iv}
1	− 13	− 14	− 5
2	5	− 34	1
3	3	− 46	− 4
4	37	− 46	− 2
5	− 121	− 111	− 4
6	− 130	− 143	− 3
7	− 290	− 205	− 1
8	− 136	− 72	− 4
9	180	35	4
10	45	40	2

convenient units which were subsequently transformed into decimal fractions of a dyne. The excesses varied in sign and size, many exceeding 100 units and the largest being 346. Many of the actual link-increments exceeded 1000 units, and as these depend on measured gravity-gradients of which the accuracy rarely exceeds 2 to 3 per cent in practice, it is considered meticulous to obtain the adjusted values of the link-increments to nearer than 10 units. The procedure thus resolves itself into one of obtaining from the excesses the corresponding correlates to the nearest 10 units.

Table 9

N	Δ	$+ \quad m' \quad -$	Δ''	$+ \quad m'' \quad -$	$+ m''' -$	$+ m^{iv} -$
8	1	39	3	15	21	6
			4	2	37	1
	2	5				
		34		17	58	7
		− 4		− 2	− 7	− 1
6	2	15	5	78	23	7
			6	115	14	10
	1	13				
	3	3				
	4	37				
		42		193	37	17
		+ 7		− 32	− 6	− 3
7	3	9	1	4	2	7
			4	2	37	1
	2	5	7	210	27	22
	5	121	9	66	31	5
		107		150	43	25
		− 15		− 21	− 6	− 4
7	4	111	1	4	2	7
			3	15	21	6
	2	5	7	210	27	22
	6	130	12	28	12	8
		14		257	8	43
		− 2		− 37	− 1	− 6
6	5	363	2	7	32	6
			6	115	14	10
	3	3	8	83	20	11
	7	290	10	51	16	7
	9	180				
		470		140	42	20
		− 78		− 23	− 7	− 3

To facilitate setting down the related first and second-remove correlates corresponding to each key correlate, it is convenient to replace every triangle in figure 7 by a correspondingly numbered dot, situated roughly at its centre of position, and to join these dots by lines representing contacts of adjacent triangles. A triangle is thus represented by a point from which radiates a number (one, two or three) of

lines to each of its first-remove points, from which again outwards radiate lines to the second-remove points. Commencing at any one point it is easy for the eye to pick up the first and second-remove points in turn. These are tabulated on the working sheets, of which table 9 shows a typical example used for the first five points in order. The first column, headed N, is used for the common divisors obtained from formulae (9) and (10) by simply subtracting the number of first-remove points from 9 in each case, since in this network $n = 3$ and $n^2 = 9$ throughout.

The second column marked Δ contains the key-point number, followed after an interval of one line by the numbers of its first-remove points in order. The third column, marked $+ m' -$, is used for computing m' from the excesses given in table 8 and equation (9). The excess for the key point is multiplied by 3 and set down opposite that point; the excess for each first-remove point is set down directly; the $+$ and $-$ columns are totalled and the aggregate sum divided by N from column 1. The result is m' for this key point. In the fourth column headed Δ'' are set down the numbers of the second-remove points in order. These are used to obtain m'', m''', m^{iv} in succession according to equation (10) by means of the subsequent columns headed $+ m'' -$, $+ m''' -$, ..., and the values previously obtained in column m' for each second-remove point.

The procedure is thus to set down the key, first-remove and second-remove points in columns 2 and 4, then the values N in column 1; compute m' for every key point and use the values so obtained in column 5 to get m'' for each point; use these latter values to get m''', and these to get m^{iv}, and so on. The values actually obtained are shown under the respective columns in table 8. The approximations to m obtained by summation $m' + m'' + m''' + m^{iv}$ are next given. The whole process for 80 points took 15 hours, an average of just over a quarter of an hour for each of the 56 gravity stations.

The adjusted link-increment values are easily obtained from the calculated m's by using equation (1), and the adjusted gravity value of each station relative to any one taken as datum can then easily be derived, and the isogams can be drawn.

A check on the accuracy of reduction is obtained by computing the residual excess for each triangle. From equations (1) and (2) it is easy to see that the residual excess d' is given by the formula d'

$$d_r' = d_r + \Sigma m_x - 3m_r,$$

which ought to be zero if the values m are accurately computed. The actual residual excesses which remained when the calculation was stopped at m^{iv} are given in table 8, column d', and are seen to be below the agreed limit of error of 10 units.

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A STUDY OF A SENSITIVE MANOMETER DUE TO PROFESSOR ALBERT GRIFFITHS

By P. C. VINCENT, M.Sc., Research Student, Birkbeck College

Communicated by Prof. Albert Griffiths, April 24, 1933

ABSTRACT. The manometer is analogous to a U-tube water manometer but the air is replaced by pure air-free water, and the water is replaced by an aqueous solution of uranine whose density differs from that of pure water. When the apparatus was made of glass, errors arose from the solution of the glass by water, which increased the density of the feeble uranine solution. The manometer functioned well when the apparatus was made of silica, which is almost insoluble in water. In order to test the working of the manometer, the pressures given directly by it were compared with those calculated from measured rates of flow along a capillary tube. As the ends of the manometer liquid become diffuse in the course of time, the rate of flow was measured by means of a coloured index, and as the index became considerably distorted a special method was devised for determining its position.

The difference of pressure measured varied in value from about 2 dyne cm.^{2} to about 20 dyne/cm.^{2}

The average numerical difference between the direct manometer readings and the calculated readings is about 1 per cent of the absolute readings. The average difference taking the sign of the difference into account is about $\frac{1}{3}$ per cent.

§ 1. INTRODUCTION

The object of the work was to test the accuracy of a sensitive manometer designed by Prof. Albert Griffiths. The manometer has been tested with differences of pressure varying in value from about 2 dyne cm.^{2} to about 20 dyne/cm.^{2} in a closed circuit containing water.

The design of the manometer will perhaps be easily understood if an analogy be made between it and the ordinary U-tube water manometer. The ordinary water manometer measures the difference between the pressure of the air on one side of the U tube and that of the air on the other side. Imagine the air to be replaced by pure air-free water, and the water to be replaced by an aqueous solution of uranine whose density differs by ρ from that of pure water.

Let h be the reading of the manometer, i.e., the difference in height in cm. between the upper extremities of the uranine solution; then the difference in pressure equals $g\rho h$ dyne/cm.^{2}

§ 2. DESCRIPTION OF MANOMETER

The manometer has placed behind it a black scale with white division marks, and the reading is made with the aid of a blue light. As the green fluorescence is plainly visible with very feeble solutions, there was a promise of a very sensitive manometer.

Obviously the two upright arms of the U tube must be at nearly the same temperature, otherwise the difference in density due to difference of temperature will mask the difference in density due to the solution of the uranine. By working in a thermostat room, and by surrounding the U tube with copper, the error due to difference of temperature was probably made negligibly small.

The apparatus was first made of glass, but unexpectedly the manometer was a complete failure. The hypothesis was made that the failure was due to the glass dissolving to relatively different extents in the water and solution in the different sides of the apparatus. Subsequent experiments proved this hypothesis to be correct.

Silica is almost insoluble in water and the glass was therefore replaced by silica. At first the silica apparatus gave very hopeful results; but in the course of time it gave results which at the lowest pressures were inconsistent to the order of 20 per cent. Ultimately this error was found to be due to a gradual diminution in the fluorescing power of the uranine solution, this diminution being caused by traces of nitric acid left in the apparatus after cleaning it. At the beginning of the research the various taps were in perfect order, and there were no channels in which traces of the injurious nitric acid could be retained. Possibly the trouble was due to the development of these channels. In the earlier experiments the usual lubricant employed was cerate of resin.

In the later experiments instead of working with absolutely pure water, water containing a trace of caustic soda was employed and the lubricant used was a solution of pure unvulcanized rubber in pure vaseline. Consistent results, presumably accurate to 1 or 2 per cent, were now obtained.

The manometer is diagrammatically represented in figure 1, and the complete apparatus is depicted diagrammatically in figure 2. *JLENFSH* suggest the U tube, *J* and *H* are the points between which there is a difference of pressure, *E* and *F* are three-way taps, *N* is an ordinary one-way tap. To introduce the manometer liquid the taps *E* and *F* are suitably arranged and a flow of the manometer liquid is passed from *E* to *F*. Further details of a necessarily complicated method of procedure are given in § 4.

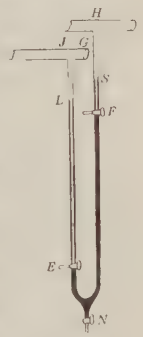

Figure 1.

The ends of the manometric liquid become fuzzy in course of time even when the pressure difference is constant. A method was therefore devised for obtaining with confidence the reading of a fuzzy end with a reasonable degree of accuracy (§ 8)

Two methods have been adopted for the determination of the differences of pressure between two points in a capillary tube. The first method

requires the employment under suitable conditions of a delicate manometer. The second involves a knowledge of both the resistance of the tube to a flow of water along it, and the rate of flow. The pressure varies as the product of the resistance into the rate of flow. Certain refinements in the procedure of the second method are described in the paper, and this method has been used as a check on the accuracy and serviceability of the first method. Comparisons suggest that both methods are reliable, to 1 or 2 per cent, and that the first method is likely to be quite as correct as the second.

The rate of flow of water in the second method was determined by the movement of a column of coloured index along a horizontal tube. This is called the index tube. The ends of the column become slightly fuzzy when the flow is very slow; they became very fuzzy under the conditions of the experiment, and as they were difficult to read, a special method was applied for determining the reading of the index (§ 12). The flow was developed by means of an electric current passing through a heating spiral, which surrounded one arm of a vertical U tube. For convenience this is called the vertical tube *OAP* of figure 2.

§ 3. THE METHOD AND THEORY OF TEST

The method and theory of testing the reliability of the manometer is as follows: (A) A definite, comparatively large pressure head of about 5 or 6 cm. of water is made to drive water through a horizontal capillary tube, and from the value of this head and of the rate of flow, the resistance of the capillary tube is calculated. In this experiment the manometer is not used. (B_1) A slow convective flow it made to take place along the same capillary tube, and from the rate of this flow and from the resistance determined by (A) the new pressure head is calculated, the head being proportional to the rate of flow. This flow is caused by a small electric heater. (B_2) The pressure head of the slow convective flow (B_1) is also measured directly by the uranine manometer. The pressure heads given by (B_1) and (B_2), being measurements of the same quantity, should substantially agree if the manometer functions properly.

P Let P be the pressure difference at the ends of the tube *JGDCBQH*, figure 2; and

V V the volume flow per second along the same tube under the pressure P.

K Then if the temperature be constant, $P = KV$, where K is a constant, called in this paper the *resistance* of the tube. If the temperature varies, then as K is a function of the temperature, and in accordance with Hoskings's* expression for

K_1 the manner in which the viscosity depends upon the temperature, K_1, the value

t_1 of K at $t_1°$ C., is given by

$$K_1 = \frac{K_0}{1 + 0{\cdot}03445\,t_1 + 0{\cdot}000235\,t_1^2},$$

* Hoskings, *Phil. Mag.* **18**, 262 (1909).

where K_0 is the constant of the tube at 0° C. It follows that if K_2 be the corresponding value of K at t_2° C., then K_0, K_2

$$\frac{K_1}{K_2} = \frac{1 + 0{\cdot}03445\,t_2 + 0{\cdot}000235\,t_2^2}{1 + 0{\cdot}03445\,t_1 + 0{\cdot}000235\,t_1^2} \qquad \ldots\ldots(1).$$

Thus if the value of K_1 be known for a temperature t_1° C., its value for a temperature t_2° C. can easily be calculated.

§ 4. APPARATUS USED FOR TEST, AND THE METHOD OF OBTAINING A SLOW FLOW ALONG THE CAPILLARY TUBE

For reasons already given and detailed later (see § 6) the apparatus used for testing the accuracy of the manometer was made of silica. The design of the apparatus is shown diagrammatically in figure 2.

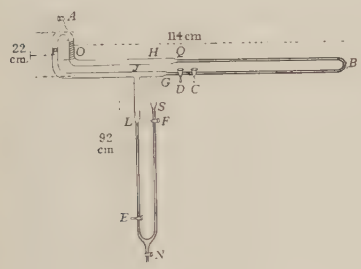

Figure 2.

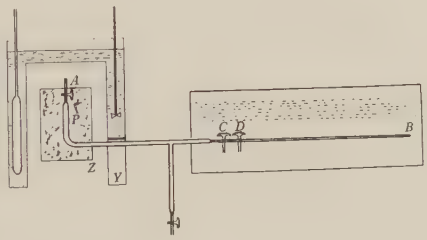

Figure 3.

The apparatus may be considered to consist of three parts: (1) the manometer tube *JLENFSH*; (2) the horizontal capillary or index tube *JGDCBQH*, on the right of the manometer, used for checking the accuracy of the manometer reading; and (3) the vertical tube *OAP*, on the left of the manometer, of the shape of an inverted U tube, and employed with the aid of an electric heater for obtaining the flow along the capillary tube.

The horizontal tube and the curved vertical tube to the left of the manometer are made up of wide bored tubing of diameter 0·5 cm. Round the vertical arm *O* is a heating spiral through which a feeble current is passed. The heating coil causes a convective flow upwards along *O*, down *P*, and round the horizontal circuit in the direction *JCBH*. The manometer liquid prevents a continuous flow round the manometer tube *JLENFSH*. The horizontal capillary or index tube to the right of the manometer is about 0·15 cm. in diameter. It contains two three-way taps *C* and *D*, by means of which a coloured index of uranine solution is introduced. The rate of movement of this index, under the influence of the convective flow, measures the rate of flow along the index tube. The manometer tube is about 0·2 cm. in diameter. The three-way taps *F* and *E* serve for the introduction of the manometric liquid.

Cleaning the apparatus. Before an experiment or a series of experiments the apparatus is cleaned with dilute nitric acid and a solution of sodium hydroxide,

and finally distilled water is allowed to flow freely through it. The neglect, at one period of the research, to neutralize the nitric acid was a most costly mistake. In course of time a small trace of acid diminishes the fluorescence of a uranine solution in such a way as to vitiate the accuracy of the manometer, especially when weak solutions are employed. A long series of observations was ruined in this way.

Filling the apparatus. It might appear at first thought that the filling of the apparatus would be easy, but in practice the operation is difficult and tedious, because no glass or silica taps can be relied upon to withstand a pressure of water after they have been frequently used. A channel always forms on the inside of the barrel of the tap. This channel on the barrel of a three-way tap is particularly troublesome; for when the tap is turned so that there is communication from one side of the tap to the other, the channel allows water to leak from the inside of the apparatus to the open air, or vice versa. To prevent this, the outlet tubes of the three-way taps were sealed with indiarubber caps ("policemen" as they are called in the trade). The fitting of the cap is an art; if the cap is first filled with water and forced over the outlet tube, as water is almost incompressible, it is very difficult to prevent the water in the tap from forcing a way through the channel of the tap into the inside of the apparatus. The three-way tap or stop-cock used was of an ordinary type. The bores of the silica tubing on either side of the tap were in the same straight line, and thus when communication was made between the two sides of the tap, the bore of the plug was in a straight line with the manometer tube. A curved passage in a plane at right angles to the bore of the plug provided an outlet to the bottom of the plug.

When certain parts of the apparatus had to be filled, it was arranged that the water should run from one supply vessel to a receiver vessel; and care was taken that the level of the water or solution should be only slightly lower in the receiving vessel than in the supply vessel. A schedule of operations was drawn up covering a dozen sheets of foolscap. This schedule is not inflicted on the reader.

The apparatus is filled by opening the upper tap *A* and applying to it a head of distilled water. By opening and closing the lower tap *N*, and by manipulating the taps *F*, *E*, *C* and *D*, the whole apparatus can be washed through and filled with air-free distilled water. Water from the same containing-vessel is used to fill and wash the apparatus and to make up the manometer solution. It was found necessary when dealing with very dilute manometer liquids to add 5 cm^3 of a 10 per cent solution of sodium hydroxide to the water in the containing vessel, that is, to the water used in filling the apparatus, and making up the manometer solution. The containing-vessel has a capacity of 10 litres, and thus the concentration is 0·00005 gm. of sodium hydroxide per cm^3.

Introducing the manometer liquid. The manometer liquid is a weak solution of uranine of known density relative to water. The part *ENF* of the manometer tube is emptied of water and a head of the manometer liquid is applied to the tap *N*. The one-way tap *N* and the three-way tap *F* are then so arranged that the uranine solution flows in at *N* and out at *F*. No solution goes above *F*. Tap *F* is then closed and tap *E* is so adjusted that the solution passes in at *N* and out at *E*.

A sufficient quantity of uranine solution is passed through the manometer to ensure that there shall be no dilution of the solution by the residue of distilled water that previously filled the manometer tube. The tap N is closed, and the taps F and E are so turned that they shut off the manometer tube and only communicate with the upper index tube. By using the head of distilled water attached to the tap A, the exit bore of the tap F can be washed clean of the manometer liquid. The exits of the taps are sealed with rubber caps; this sealing is of vital importance. The taps F and E now separate the upper horizontal circuit containing distilled water from the manometer tube containing a weak solution of uranine, so the upper tap A may be left open and in communication with a reservoir of distilled water and yet leave the manometer liquid undisturbed. This allows the effects due to temperature, etc. to settle down before observations are made. The exit tap N is closed with a rubber cap and finally sealed with mercury, whilst throughout an experiment the tap A is left in communication with the reservoir of distilled water.

Introducing the index. The index, a column of uranine solution, is introduced into the index tube by means of the three-way taps C and D. The solution flows in at the port of C, up the vertical bore of the tap, along the capillary tube CD, and out at the port of D. The uranine supply is cut off and the taps C and D are turned through 90°, so that an uninterrupted flow can take place along the index tube. After the head of the index has travelled far enough along the tube, the length of the index can be shortened at will by washing through with distilled water from C to D.

The vertical U *tube and heating coil.* The two arms of the vertical tube OAP are embedded in asbestos wool. The vertical tube, copper block* and asbestos wool are enclosed in a copper cylinder Z, around which a water-jacket Y is placed which completely envelops it. The water within the jacket is electrically heated and stirred, and maintained at a constant temperature by a delicate thermostat control not indicated in figure 3.

The elimination of irregularities of temperature. All parts of the apparatus excepting the index tube, which is immersed in a water bath, are enclosed in copper shields.

The reading-scales. Beneath the horizontal index tube and behind the manometer tube are placed black centimetre scales lined out with white. The index scale is made water-proof as it is immersed in a tank of water. The manometer scale is marked out on a strip of sheet copper, which has been blackened with ammonium sulphide. Under the conditions of the experiment scales consisting of white lines on a black background are preferable to ordinary scales.

The situation of the index tube. The index tube is immersed in water contained in a large galvanized iron tank. The water in the tank can be stirred by an electric stirrer. Cooling due to the evaporation of the water in the tank is checked by

* A block of copper measuring 8 × 4 × 1 cm. is placed about 1 cm. from the heating coil. This is introduced to increase the speed of attainment of a steady temperature-gradient between the two vertical arms. The same effect can probably be attained by placing the two vertical arms closer together.

covering the water with a wooden float that has been soaked in paraffin wax. Mercury thermometers are placed vertically in the tank.

The heating current. The heating current through the coil, figure 2, is obtained from two accumulators, and is controlled by a 130-ohm variable rheostat. The current is measured on a millivoltmeter placed across the terminals of a 4-ohm shunt. The resistance of the heating-coil is about 113 ohms. The current required to maintain a pressure head measurable by the manometer, and of the order of 3 or 4 dyne/cm.^{2} was determined by a series of preliminary experiments and was found to be about 24 mA.

§ 5. EFFECT OF IRREGULARITIES IN TEMPERATURE

The current required to maintain a constant manometer difference is found to depend upon the temperature of the water-jacket enclosing the heating portion of the apparatus. The main reason for this is undoubtedly the fact that the coefficient of cubical expansion of water varies so considerably with change of temperature. A numerical example will make this clear. It may be mentioned that in a certain experiment it was estimated that the difference of temperature between the two arms of the vertical heating tube was 1·5° C. Let the hypothesis be made that the difference in temperature between the two arms of the vertical heating tube is independent of the temperature of the enclosure; in the case of the apparatus under consideration this is approximately true. Consider the case in which the temperature of one arm is 20·5° C., and the temperature of the other arm is 22·0° C., the difference of density as given by ordinary standard tables is 0·000329 gm./cm.^{3} Now consider the case in which each arm is 1° higher in temperature, the temperature of one arm being 21·5° C. and the temperature of the other being 23·0° C.; the difference of density is now 0·000344 gm. cm.^{3} Thus an increase of 1° in the average temperature of the vertical heating tube increases the driving head by 15 parts in 329, that is, by $4\frac{1}{2}$ per cent, the current being constant.

§ 6. PRELIMINARY EXPERIMENTS WITH GLASS APPARATUS

Originally the manometer was made of glass and formed part of a glass apparatus, which was similar in design to the silica apparatus shown in figure 2. Although in the experimental work with the glass apparatus the flow along the index tube was normal—constant for a steady heating current and increasing with an increase of current—yet the manometer gave readings which were altogether unexpected. To simplify matters, and in the hope of determining the cause of the remarkable readings, it was decided to experiment without the heating-current.

Experiments without the heating-current. In the first experiment the manometer solution was introduced as shown in figure 1, and the solution flowed considerably past the equilibrium position, i.e., the position where the extremities of the uranine columns are level. Thinking that a mistake had been made, the apparatus was emptied and a new manometer solution was introduced. This time the difference between the levels of the uranine columns was at first ·63 cm.; it then dropped

to zero and later became − 27 cm.; it then came back to zero and rose ultimately to + 48 cm. This experiment was also stopped whilst the movement was in progress. Tables of solubility of glass were consulted and it seemed quite reasonable to suppose that the odd results were due to the glass from the inner surface of the tube dissolving in the water and masking the action expected from the density difference between the water and the uranine solution.

The first experiment can be explained by assuming that the glass of the tube *FN*, figure 1, dissolved more rapidly per cubic centimetre of water than the glass of the tube *EL*. An explanation of the second experiment is not so simple. It can be obtained by assuming that the water in the horizontal part of the apparatus near the top of the tube *ELJ* dissolved glass fairly abundantly, and that at a certain moment a flow was engendered down the tube *JLE* and maintained by a supply of comparatively dense solution from the horizontal tube *JG*. A third experiment gave similar results to the second, and a fourth experiment gave similar results to the first.

To simplify the conditions still more, the manometer was separated from the horizontal part of the apparatus, and its upper ends were connected by an inverted U tube. In four successive experiments there was a flow consistent with the hypothesis that the water became denser in the arm *FN* than in the arm *EL*, figure 1. By turning the manometer through 180° about a vertical axis midway between the two tubes, it was proved that the effect observed was not due to a difference of temperature.

Results. In the first experiment under the simplified conditions there was the expected fall of the manometer due to the initial head of uranine solution, but the movement continued until the uranine solution was 4 cm. higher in the arm *EL* than in the arm *FN*. In the second experiment a similar movement took place until the difference was 10 cm. The difference was still increasing; and to test whether it was due to spatial inequality of temperature the apparatus was then turned through 180° about a vertical axis midway between the tubes. The movement continued in the same direction, and the difference in level was ultimately 16·5 cm.

The strength of the uranine solution in these experiments was 0·125 gm./litre, and to increase the sensitivity of the apparatus it was reduced to 0·0125 gm./litre.

In the third experiment there was a movement of 120 cm. down the arm *FN* and up the arm *EL*, the uranine solution being at the top of the apparatus at the conclusion of the observations. In the fourth experiment the uranine solution fell in the arm *FN* and rose in the arm *EL* until there was a difference of 77·5 cm. between its extremities.

The movement in each experiment was in the direction expected from the initial head of uranine solution, but greater than the head of uranine solution would account for, and it suggested a greater solubility of the glass in the tube *FN* than in the tube *EL*.

Experiments with tubes of the same material but of different diameters. Since the ratio of the volume of a cylindrical tube to the area of its inner curved surface

varies directly as the radius, it follows that the narrower the tube the greater per cm^3 will be the rate of solution of the glass in the water within the tube; and if the manometer arms are of the same material but of different diameters, the flow should be down the narrower tube. This is exactly what did take place with a specially constructed piece of apparatus. The U tube and the manometer were separated and the ends of the manometer tube were connected by an elongated U tube, about 50 cm. long, one tube of which was 5 mm. and the other 2 mm. in diameter.

In the first experiment there was a movement of 93 cm. up the side of the wide tube. Many additional experiments which it is impossible to describe briefly were performed, and all the results obtained suggest that the rate of increase in the density of the water in the narrow glass tube is greater than the rate of increase in the wide tube.

§ 7. THE DENSITY OF THE MANOMETER SOLUTION

The method used in the determination of the difference between the density of the manometer fluid, a weak solution of uranine, and the density of pure water at the same temperature, was that of finding the change in weight of a sinker, approximately 1152 cm^3 in volume, when suspended in water and when suspended in a solution of uranine of known concentration, the weight of the sinker in air being known. The density difference was assumed to be proportional to the concentration*. From the determined density difference of a known concentration the density difference of a weak concentration was calculated.

The water and solution were well stirred between the weighings. The temperature was observed and allowance was made for changes in weight due to changes in temperature. As the temperature changes make the determination of the density difference difficult, it is important to keep the temperature of the liquid in which the sinker is immersed as uniform as possible; to do this the vessel which contained first the pure water and afterwards the uranine solution was surrounded by a water bath situated in a box lined with cork dust. To prevent cooling by evaporation, the surface of the liquid containing the sinker was covered with a layer of B.P. paraffin, and the temperature of this liquid could be maintained still more constant by the careful addition of warm water to the water-bath enclosure.

The results of the experiment of July 1931 will indicate the method. As speed was important the method of swings was used in the weighings, the sensitivity of the balance being 1·5 divisions per milligram. As the temperatures of the initial and final weighings were different, the weights were reduced to a standard temperature. The change in weight of the immersed sinker corresponding to a change of temperature was found to be 0·21 gm. C., measured on a Beckmann thermometer.

* A. and C. H. Griffiths, *Proc. Phys. Soc.* **33**, 231 (1921).

The weight of the sinker immersed in water was ...	33·96 gm.
The weight of the sinker immersed in uranine solution (allowing for corrections) was	33·2295 gm.
The loss of weight of the sinker was	0·7305 gm.
The volume of the sinker was	1151·8 cm.^{3}
The volume of the solution in which the sinker was immersed was	12·5 litres
The weight of commercial uranine used in solution was	15·0 gm.

From the above results the density difference between a solution of uranine of concentration 1 gm./litre and pure water was found to be 0·0005283 gm./cm.^{3} at 20° C. This value was probably correct to the third significant figure. Determinations of the density difference between the manometer liquid and water were made for each sample of uranine used; this difference was found to depend upon the sample. The calculated density difference due to a concentration of 1 gm./litre was as follows:

Experiment	Uranine	Density difference
July 1931	Commercial	0·0005283 gm./cm.^{3}
August 1932	Pure	0·0004196 gm./cm.^{3}

Commercial uranine from the same sample, that had been carefully kept in a tightly corked bottle, and from which the density-difference determinations had been made, was used throughout the first series of experiments. Pure uranine from the same sample, that had been kept in a tightly corked bottle, and from which the second density-difference determinations were made, was used throughout the second series of experiments.

The influence of temperature on the difference between the density of the manometer liquid and that of water.

Let d_1 be the density of water at t_1° C.; $d_1, t_1°$
D_1 the density of the solution at t_1° C.; D_1
v_1 the specific volume of water at t_1° C.; v_1
V_1 the specific volume of the solution at t_1° C.; V_1
d_2, D_2, v_2, V_2 be the corresponding quantities at t_2° C.; $d_2, D_2, v_2, V_2, t_2°$
and let t_2 be taken as less than t_1.

Insomuch that a weak solution must expand for a change of temperature by nearly the same amount as pure water, it is clear that

$$v_1/V_1 = v_2/V_2 \text{ and } D_1/d_1 = D_2/d_2, \text{ whence } (D_2 - d_2) = (D_1 - d_1)\, d_2/d_1.$$

If ρ_2 is the difference of density between the weak uranine solution and the water at a temperature t_2, and ρ_1 is the corresponding density difference at t_1, then, ρ_2 ρ_1

$$\rho_2 = \rho_1 d_2/d_1.$$

In the experiments the ratio of d_2 to d_1 was little different from unity. Perhaps the point will be made clearer if we assume an approximate coefficient of expansion y of water in the neighbourhood of 20° C., the temperature of the manometer. y

Let $y = 0{\cdot}0002$, then $d_2/d_1 = v_1/v_2 = 1 + (t_1 - t_2)\,y$.

If $(t_1 - t_2) = 2^\circ$ C., an extreme difference of temperature for the experimental work, then

$$d_2/d_1 = 1{\cdot}0004 \text{ approximately.}$$

Thus $d_2 = 1{\cdot}0004\,d_1$, and if ρ_2 be taken equal to ρ_1 the error is less than $\frac{1}{2\cdot7}$ per cent.

§ 8. A METHOD OF DETERMINING THE MANOMETER LEVELS

The uranine solution in the manometer was illuminated by a blue lamp. There is no sharp surface of separation between the uranine solution and the water above it. The uranine diffuses into the water and there is a centimetre or more where the uranine is gradually merging into the pure water. Both heads of the manometer column have substantially the same appearance, and it is possible to take readings of corresponding points; the difference between these readings should give the true manometer head. In practice the method proves difficult, and a method was devised which ensured both accuracy and ease, and gave a reading based on a great number of independent observations.

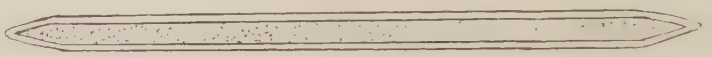

Figure 4.

A series of capillary tubes, figure 4, of the same diameter as the manometer tube, was filled with uranine solutions of graded concentrations. The uranine solution in tube 1 was of the same strength as the strongest manometer solution. The comparative concentrations of the other members of the series are detailed in Table 1.

Table 1

Tube	Strength	Tube	Strength	Tube	Strength
1	1·0	8	0·3	E	0·05
2	0·9	9	0·2	F	0·04
3	0·8	10	0·1	G	0·03
4	0·7	A	0·09	H	0·02
5	0·6	B	0·08	L	0·01
6	0·5	C	0·07		
7	0·4	D	0·06		

Each concentration tube was placed in turn against that part of the manometer where the uranine solution is slowly diffusing into the water above it, and by means of the blue lamp a series of positions of corresponding uranine concentrations was found upon the black manometer scale. A table of these readings and of the corresponding concentrations of the manometer solution, as indicated by the concentration-tubes, was made. An example of a series of readings of the same manometer level taken by independent observers by the concentration-tube method is detailed in table 2.

Table 2. Manometer readings and concentrations

Tube	Strength	Observer A	Observer A	Observer B	Observer B
		Level 1	Level 2	Level 1	Level 2
8	0·30	30·0	30·0	31·2	31·2
9	0·20	31·0	31·0	32·2	32·2
10	0·10	33·3	33·5	33·7	33·5
A	0·09	33·3	33·5	33·5	33·5
B	0·08	33·5	33·7	33·5	34·0
C	0·07	33·8	34·0	34·0	34·0
D	0·06	33·9	34·1	34·0	34·5
E	0·05	34·3	34·4	34·5	34·5
F	0·04	34·6	34·7	—	—
G	0·03	35·2	35·0	35·0	35·0
H	0·02	35·8	35·5	—	—
L	0·01	37·5	37·0	36·5	36·5
True levels		31·76	31·74	32·47	32·42
Difference		− 0·02		− 0·05	

Method of obtaining the true manometer level from a series of observations. Let C_0 be the maximum concentration of the manometer liquid, and consider any length dh of the diffused manometer extremity at which the concentration is C, then

C_0
h, C

$$Cdh/C_0$$

is the equivalent length of a manometer element at full strength, i.e., at concentration C_0.

Thus the equivalent length at full strength to the manometer column above a point whose reading is h_1 is

$$\int_{h_1}^{\infty} \frac{Cdh}{C_0};$$

or, if h_2 be the point at which the uranine is present in the manometer liquid in negligible amount, and if h_1 be a reading at which the concentration is C_0, then the true reading of the manometer is

h_2
h_1

$$\int_{h_1}^{h_2} \frac{Cdh}{C_0}.$$

The integration is performed with the aid of a graph and squared paper.

§ 9. THE INITIAL MANOMETER LEVEL

When experiments were made with the glass apparatus, it was found that even when no current was operating the levels of the manometer extremities differed considerably. It was important therefore to be sure that in the case of the silica apparatus there was no initial manometer head, that is, that the extremities of the manometer solution were at the same level when the current had been cut off and the manometer had been allowed to come to an equilibrium position. This was particularly important in the case of the very dilute manometer liquids.

The apparatus was washed and filled with distilled water, which in the case of

the dilute manometer solutions contained a trace of sodium hydroxide. A current was put on for about twelve hours, sufficient to keep the manometer liquid between the limits of the taps F and E when these taps were open to the manometer movement. During the twelve hours, however, the taps F and E were turned so that the manometer was cut off from the effect of the density difference due to the heating current. At the expiration of the twelve hours the taps F and E were turned so as to bring the density difference into action upon the manometer. At the same time the current was lowered, usually in one stage, but in the case of the very dilute manometer solution in seven stages of one and a half hours each. A slow movement of the manometer has the advantages that the extremities are short, symmetrical, and less diffuse. As a result of lowering the current to zero the manometer fell until its extremities were at the same height in the two arms. The positions of the manometer levels were found by the concentration-tube method already described.

The results of various tests with manometer solutions of different concentrations are detailed in table 3. The average difference is 0·06 cm. The manometer was generally used with a difference of level of about 50 cm.

Table 3

Date 1931	Manometer strength (gm./litre)	Manometer level left	Manometer level right	Difference (cm.)	Observer	Drop of current (stages)
July 1	One	33·66	33·60	+ 0·06	A	One
,, 1	One	32·27	32·29	− 0·02	B	One
,, 1	One	32·97	32·97	− 0·00	A	One
,, 29	0·4	31·21	31·44	− 0·23	B	One
,, 31	0·4	33·13	33·23	− 0·10	A	One
Aug. 2	0·4	31·76	31·74	+ 0·02	A	One
,, 2	0·4	32·47	32·42	+ 0·05	C	One
,, 2	0·4	31·73	31·91	− 0·18	B	One
,, 6	0·2	31·79	31·70	+ 0·09	A	One
,, 8	0·2	31·69	31·76	− 0·07	A	One
Nov. 11	0·125	32·15	32·27	− 0·12	A	Seven stages
,, 11	0·125	32·35	32·53	− 0·18	A	each 1½ hours

§ 10. RAPID-FLOW EXPERIMENTS*

t_1 Let t_1 be the temperature of the rapid flow experiments;

P_1 P_1 the pressure in dynes/cm^2 at t_1° C.;

V_1 V_1 the volume flow cm^3/sec. at t_1° C.; and

K_1 K_1 the resistance of the index tube (the value of K) at t_1° C.

Then

$$P_1 = K_1 V_1.$$

P_1 and V_1 are measured directly, and from their values K_1 is found.

* See § 3.

The measurement of K_1, the resistance of the index tube. The resistance of the index tube was measured directly by means of a known pressure head and a measured flow. The tube was separated from the apparatus at points between JG and HQ, see figure 2. This tube $JDCBQH$ had a bore of such magnitude, that in order to make the energy correction negligibly small it was found advisable to have a head as small as 5 or 6 cm. of water.

X and Y, figure 5, are glass pneumatic troughs about 30 cm. in diameter, in the sides of which holes have been bored in order to provide connection with the tube $JCDBQH$. The water in each trough was covered with a layer of medicinal paraffin oil. This prevents evaporation and thus makes for reliability in an estimation of a change of volume by means of the change in weight, and further, the absence of evaporation makes the temperature more constant. The two arms PQ and RS were attached to a vertical slider actuated by a screw, and the ends Q and S were provided with needle points. White paper was placed at the bottom of each trough and light was cast on the trough from above. When the arms PQ and RS were lowered a characteristic bright spot was formed on the paper at the moment of

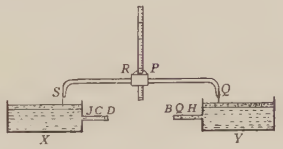

Figure 5. Diagrammatic sketch of the apparatus.

contact of the needle point with the surface of the paraffin oil. The readings of the same level were often absolutely the same, and they very rarely varied by as much as 0·002 mm. The correction to be applied because the needle point of Q was not at the same height as that of S, and also for the fact that there were not necessarily layers of the same thickness of paraffin oil in each trough, was made by connecting the troughs by a wide tube so as to produce equilibrium between the two troughs, before making appropriate measurements. The volume of the liquid which passed from Y to X was determined by weighing X on a strong balance before and after the flow.

In a typical experiment the total flow of water was 325 gm., the rate of flow along the capillary tube was 2·7 cm. per minute, the kinetic energy correction was less than 0·1 per cent, and the correction for the auxiliary tubes connecting the troughs to the capillary tubes was less than 0·3 per cent. Three determinations of K were made, two with a flow in one direction and one with a flow in the other direction; the values of K were reduced to a standard temperature of 20° C., and the average value of K_1 was taken as correct.

		Value of K_1
Results.	1st experiment, direct flow	127652
	2nd experiment, direct flow	127204
	3rd experiment, reverse flow	127619
	Average	127492

K_t The average value of K_1 at 20° C. was taken to be 127500. The value of K_t, the resistance at $t°$ C., is given by

$$K_t = 127500 \times \frac{1 + 0{\cdot}03445 \times 20 + 0{\cdot}000235 \times 20^2}{1 + 0{\cdot}03445 \times t + 0{\cdot}000235 \times t^2}$$

$$= \frac{227300}{1 + 0{\cdot}03445 \times t + 0{\cdot}000235 \times t^2}.$$

Experiment of December 27, 1930.

h_0 h_0, the initial head was 6·517 cm.;
h_1 h_1, the final head was 5·520 cm.;
M M, the total flow was 325·7 gm.;
t t, the temperature of the water was 19·46° C.;
ρ ρ, the density of the water was 0·998 gm./cm.^{3};
Q Q, the total flow was M/ρ cm.^{3};
T T, the time of total flow was 7200 sec.;
a a, the radius of the index tube was 0·0735 cm.

The equation for K, uncorrected for the kinetic energy of flow, is

$$K = \frac{\rho g (h_0 - h_1)}{V \log (h_0/h_1)}.$$

The value of K, corrected for the kinetic energy of flow, is given very approximately by

$$K = \frac{1}{v}\left[\frac{\rho g (h_0 - h_1)}{\log_e (h_0/h_1)} - \frac{v^2 \rho}{a^4 \pi^2}\right].$$

Experiment of December 27, 1930.

K uncorrected was 129800 at 19·46° C. The kinetic energy correction given by $\rho V/\pi^2 a^4$ was 156; this is relatively small. The corrected value of K was then 129644. K reduced to a standard temperature of 20° C. became 127944. The correction for the resistance of the auxiliary tubes was 325, obtained from the expression $8l/\pi r^4$, where r is 0·26 cm. and l is 56 cm.

The final value of K was 127619.

§ 11. SLOW-FLOW EXPERIMENT

Let t_2, P_2, V_2 and K_2 be the corresponding values of t_1, P_1, V_1 and K_1 for the slow-flow experiments, then

$$P_2 = K_2 V_2.$$

Since the evidence* is in favour of the viscosity having the same value at low rates of shear as at high rates, we may by using equation (1) write this as follows:

$$P_2 = K_1 V_2 \frac{1 + 0{\cdot}03445\, t_1 + 0{\cdot}000235\, t_1^2}{1 + 0{\cdot}03445\, t_2 + 0{\cdot}000235\, t_2^2}$$

or

$$P_2 = V_2 \frac{227300}{1 + 0{\cdot}03445\, t_2 + 0{\cdot}000235\, t_2^2} \qquad \text{.....(2).}$$

* A. and C. H. Griffiths, *Proc. Phys. Soc.* **33**, 231 (1921).

This equation determines P_2, for the value of K_1 has been determined experimentally, and V_2 and t_2 are measured directly.

Method of making a slow-flow experiment. The apparatus is cleaned and filled. After the filling the manometer taps are so turned that they separate the horizontal circuit from the manometer. The tap A, figure 2, is left open and in communication with a reservoir of distilled water. A pressure head is used so that the extremities of the manometer column are well out of the taps. A current of sufficient strength to maintain this pressure head is passed through the heating coil; this current is determined by a series of preliminary experiments. The water baths of the index tube and vertical tube may be gently stirred, and thermometers are placed vertically in these baths. A thermometer is also placed close to the centre of the manometer scale. The index taps C and D are turned so as to prevent any movement of the index. The apparatus is then left about twelve hours to ensure steady conditions.

At the close of the waiting period the manometer taps are turned so that the manometer difference adjusts itself to the pressure arising from the convective flow due to the heating current. When the manometer reaches a steady state, the index taps C and D are turned so as to allow a movement of the index along the horizontal tube. The exact time of opening these taps is noted.

The apparatus is now so arranged that the manometer liquid shall register any difference of pressure arising out of a density difference within the arms of the vertical tube due to the heating effect of the current, and the movement of the index should indicate the rate of movement of the convective flow along the horizontal tube.

The whole apparatus is in a double-walled room. The position of the index and the manometer levels, the temperatures of the water baths of the horizontal and vertical tubes, and the temperature of the manometer are read at regular intervals. From these, the volume flow per second through the index tube, the pressure as indicated by the difference in manometer levels, and the temperature of the water in the index tube are known. The current strength is checked at regular intervals. The position of the index and of the manometer levels is judged by the methods already explained.

§ 12. THE READING OF THE INDEX

The positions of equal colour-intensity in the index and the corresponding concentrations in the graded concentration tubes are noted. A figure is then drawn on squared paper in which the readings of the positions of the tubes as abscissae are plotted against the concentrations as ordinates. A figure $ABCDE$, figure 6, is thus obtained. The figure is cut out and its centre of gravity obtained by balancing. The ordinate of the centre of gravity is taken as the reading of the index.

An account of the reasons why Prof. Griffiths suggested the centre-of-gravity method may not be out of place. Let us, in the first place, suppose that there is a coloured index of uranine solution in an infinitely long horizontal tube of uniform

bore containing water at rest. Let it be assumed that the only cause of the elongation of the index is diffusion, and that at a given moment the density of the solution is uniform over a cross-section at right angles to the length of the tube. For purposes of mathematical analysis the coloured index may be imagined to consist of an indefinitely large number of small elements bounded by vertical planes normal to the axis of the tube. The uranine in each element may be supposed to diffuse symmetrically, and therefore there can be no change, arising from diffusion, in the position of the centre of gravity of the uranine originally in the element. It follows then that as the position of the centre of gravity of each element is unaffected by diffusion, the position of the centre of gravity of the whole index is unaffected by diffusion, i.e. the centre of gravity of the uranine index remains exactly in the same position and is independent of diffusion.

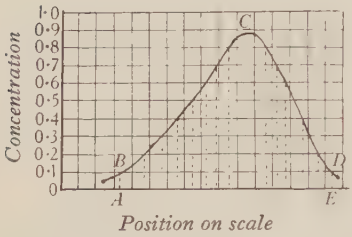

Figure 6.

Figure 7.

Now let us consider the case when the water is not at rest. An element of the uranine now experiences a movement due to two causes, one being the movement of the water in a given direction, and the other being due to diffusion, or molecular movement.

Let AB represent the horizontal tube along which the steady flow of water is taking place, and let p, q indicate two adjacent vertical planes normal to the
x_2, x_1 direction of flow, at a distance $(x_2 - x_1)$ apart. Suppose the bore of the horizontal tube to be so small that in spite of the flow the density may be considered uniform over any cross-section such as p. Let PQR represent the cross-section of the bore,
a and da an element of area at S.

c_1 Let c_1 be the concentration at the cross-section p;

k k the coefficient of diffusion of the solution;

v v the normal component of the velocity of the flow at S, which is not constant over the cross-section.

t The quantity of uranine crossing the element da in time dt may be written

$$\left[\int vc_1 da - k\frac{dc_1}{dx}\int da\right] dt,$$

the integration being taken over the whole cross-sectional area. It is assumed that c_1 is uniform over the plane A, the intersection of p with the bore of the tube.

Then the quantity of uranine entering through p into the space between p and q equals

$$\left[c_1 \int v\,da - k\frac{dc_1}{dx}\int da\right] dt,$$

the integration being taken over the whole cross-section.

Let A be the area of the cross-section, and V the volume flow per second, then the quantity of uranine crossing p from left to right, the direction of the flow, may be written A, V

$$[c_1 V - kA\, dc_1/dx]\, dt.$$

Let U be the average velocity of the linear flow along the tube, U being defined as V/A; then the quantity of uranine entering through p into the space between p and q equals U

$$A\,[c_1 U - k\, dc_1/dx]\, dt.$$

The quantity of uranine crossing q from left to right in time dt equals

$$A\,[c_2 U - k\,\{dc_1/dx + (x_2 - x_1)\, d^2c_1/dx^2\}]\, dt.$$

The rate of increase of the quantity of uranine per unit time between p and q therefore equals

$$AU(c_2 - c_1) + Ak(x_2 - x_1)\, d^2c_1/dx^2.$$

That is, the rate of increase of uranine per unit volume per unit time in the element between the cross-sections p and q equals

$$\frac{AU(c_2 - c_1) + Ak(x_2 - x_1)\, d^2c_1/dx^2}{A(x_2 - x_1)},$$

that is

$$U\,dc/dx + k\,d^2c/dx^2,$$

or

$$\frac{dc}{dt} = U\frac{dc}{dx} + k\frac{d^2c}{dx^2}.$$

This equation proves that there is no necessity to know the character of the flow along the capillary, so long as it is steady and uniform. The flow may be of the parabolic type or may be any function of the position of S in PQR; in all cases the index varies in character in course of time, just as it would if the water moved through the tube with a constant velocity at all points in the tube.

A mental picture of the flow is obtained if we imagine the liquid to be replaced by a transparent solid rod moving along the tube. Now moving the rod will not appreciably affect the diffusion in relation to the rod, and the centre of gravity of the index will therefore remain in the same part of the rod; and thus if the rod move with velocity U, the centre of gravity will move at the same speed. It may be noted that there is no need for the index to be symmetrical.

So far we have only considered the elongation of the index as caused by diffusion. As a matter of fact the elongation of the index may be due to gravity. The movement due to gravity decreases with the increase in dilution, and also diminishes with a diminution in the radius of the capillary tube, as the effect of the viscosity of the water increases with the diminution in radius.

Thus when the diameter of the capillary tube is sufficiently small, or the concentration of the index solution sufficiently small, or, to be more general, some

unknown function of the diameter, concentration, and concentration-gradient is sufficiently small, gravity may be neglected in comparison with diffusion.

A number of experiments have been performed which prove that a weakening in the concentration of the solution or a diminution in the diameter of a tube does actually make the effect due to gravity appreciably small.

To compare the effect of a combination of diffusion and gravity-convection with the effect due to diffusion alone, it is convenient to compare the transmission of uranine along a vertical tube originally containing water with that along a horizontal tube. It is quite easy to carry out rough experiments. In one series a Woulff's bottle was employed. To study the horizontal transmission two tubes were fixed in the horizontal necks, the Woulff's bottle was filled with water and the water was allowed to fill the tubes. The tubes were then sealed with indiarubber caps. The water in the Woulff's bottle was then replaced by uranine solution. A third tube was filled with water, one end being closed. The water stays in position even when the tube is held vertical with the opening downwards. It is thus easy to place the vertical tube in position with the lower end in the uranine solution.

A different apparatus has been used in which the transmission takes place down the tube. With a uranine solution of the same concentration as that used for the index, i.e. 0·25 gm./litre, and a tube of bore 1·5 mm., there was no substantial difference between the horizontal and vertical transmissions. With a uranine solution of concentration 5 gm./litre, and tubes of bore 1·5 mm., the transmission horizontally was distinctly bigger than the pure diffusion upwards. The transmission down the vertical tube was considerable. With a uranine solution of concentration 5 gm./litre, and tubes of bore 0·5 mm., the transmission vertically downwards was very much less than that down the tube of diameter 1·5 mm.; and the horizontal transmission was little different from the pure diffusion upwards. In practice, in the course of time, the gravity-effect automatically becomes relatively less important.

As has already been explained, the density of the uranine at various points is determined with the assistance of a series of graded proof tubes, as they may be called. Numerous readings are taken, and individual errors tend to average out. The method requires a long time for a complete reading. In practice the position of the index may be obtained to a fair degree of accuracy by taking the mean of readings in the neighbourhood of the points of inflexion of the graph, figure 6. It is not proper to take the mean of the whole number of readings, as this gives too much weight to the readings of the proof tubes filled with weak solutions. This method does not give the same position of the index as the centre-of-gravity method, but the difference between two positions of the index obtained by the two methods is roughly the same.

§ 13. INTERPRETATION OF THE EXPERIMENTAL RESULTS

To find for one complete experiment the average value of the manometer difference, the mean of two consecutive readings was multiplied by the time interval between the readings. These products were then totalled for the whole experiment and divided by the complete time interval between the first and last reading of the manometer. This value should give the average value of the manometer difference throughout the experiment. A corresponding method was adopted with the temperature-readings.

Experiment of February 6, 1932. The average value of the manometer difference measured directly was 49·17 cm.

The average temperature t_2 of flow was 21·2° C.

The average flow per second V_2 was 0·00002052 cm.^{3} The flow per second was obtained by taking the initial and final positions of the index on the calibration graph, and dividing the volume thus found by the total time.

Substituting in equation 2 the values of V_2 and t_2, we have

$$P_2 = 2{\cdot}54 \text{ dyne/cm.}^2$$

If we consider the equation

$$P_2 = hg\rho,$$

where h is the manometer difference in centimetres and ρ is the density difference between the uranine solution and the water in the manometer, i.e. 0·00005245 gm., then $h = 49{\cdot}3$ cm. h, ρ

As has been stated above, the manometer difference measured directly by the concentration tubes was 49·17 cm. Thus there is a difference between the measured and calculated manometer head of 0·2 cm.

The correction for the manometer movement. A correction has to be applied to the measurement of the manometer difference because of the slight movement of the manometer during an experiment.

Let r be the radius of the manometer tube, i.e. 0·0944 cm.; r

l the length of the manometer tube, i.e. 169 cm.; l

η the coefficient of viscosity of the manometer solution at the temperature of the manometer. This is substantially the same as that of pure water. η

For a manometer movement dh performed in time dt

$$V = A\,dh/2\,dt.$$

Then the difference of pressure between the two ends of the manometer at any moment, where h is the average measured manometer difference during the movement dh, equals

$$g\rho h + 4l\eta\,dh/r^2\,dt.$$

The average pressure T over a time equals T

$$g\rho \int \frac{h\,dt}{T} + \left[\int \frac{4l\eta}{r^2} \frac{dh}{dt}\,dt \right] \frac{l}{T}.$$

If P be the corrected pressure in dynes, then P

$$P = (g\rho \times \text{average difference of manometer levels}) + \frac{4l\eta}{r^2} \int_{h_0}^{h_r} \frac{dh}{T},$$

h_0, h_τ where h_0 is the initial and h_τ the final manometer difference in time T.

$$P = g\rho h + \frac{4l\eta}{r^2}\frac{(h_\tau - h_0)}{T}$$

$$= (g\rho \times \text{average difference of manometer levels}) + \frac{4l\eta}{r^2}\frac{(h_\tau - h_0)}{T}.$$

The above proves that the corrected reading of the manometer equals the average difference of level plus $4l\eta\, r^2$ multiplied by the average rate of change with respect to time of the manometer reading, however inconstant the rate of variation may be. Inasmuch as the correction is small, no great accuracy is required in the values of l and r.

As an example of the correction for the manometer movement consider the experiment of February 6, 1932.

The initial manometer difference was 49·20 cm.

The final manometer difference was 49·72 cm.

The change in manometer difference was + 0·52 cm.

The total time of flow T was 1080 minutes.

The temperature of the manometer was 21·8° C.

The coefficient of viscosity was 0·00963.

The density difference of the manometer solution was 0·00005245 gm. cm.^{3}

If D be the correction in centimetres, then

$$D = 4l\eta\,(h_\tau - h_0)\, r^2/g\rho T.$$

Substituting the above values and changing the minutes to seconds, we obtain

$$D = 0{\cdot}12 \text{ cm. approximately.}$$

Therefore + 0·12 cm. has to be added to the average manometer difference of the experiment, i.e. 49·05 cm., to obtain the true manometer height; this equals 49·17 cm. The average correction for the manometer movement taken over the whole range of experiments was − 0·07 cm. This on an average manometer difference of 40 cm. is a correction of about 0·14 per cent.

Various density differences were experimented with, and the results were tabulated as in the following example:

Date. July 11, 1931. Time of flow 171·3 minutes.

Total flow 1·718 cm.^{3} Rate of flow 1672 × 10^{-7} cm.^{3}/sec.

Mean temperature during flow 22·15° C.

a Measured difference a of manometer levels 38·92 cm.

b Calculated difference b of manometer levels 39·14 cm.

$a - b = -0{\cdot}22$ cm.

Current in quarter-milliamperes = 248. Density difference × 10^3 = ·5283 gm./cm.^{3}

c a expressed in dyne/cm.^{2} = c = 20·17.

d b expressed in dyne/cm.^{2} = d = 20·29.

$c - d = -0{\cdot}12$ dyne/cm.^{2}

§ 14. PRECAUTIONS WITH WEAK SOLUTIONS

It was found during an unfortunate period of work that with very dilute solutions of concentration-difference 0·00005 gm./cm.^{3}, the extremities of the uranine columns became fainter in the course of time, and to an unequal extent; and that when there was no heating current the levels did not come the same. This was found to arise from a definite diminution in the fluorescing power of the manometer solution, and was apparently due to the chemical action of traces of nitric acid left in the apparatus. The taps had become worn in the course of time, and there were the usual channels due to the turning of the plug in the barrel; thus there were many places where traces of acid could remain.

The trouble vanished when a trace of caustic soda was added to the water used in the experiments. At this stage, as an additional precaution, the taps were reground; also a lubricant made up of a solution of pure unvulcanized rubber in pure vaseline was used. This solution was most satisfactory both as a lubricant and as a seal.

During the preparation of an experiment, after the apparatus had been washed with dilute nitric acid, the manometer taps were removed, washed again with distilled water and dried, washed with a solution of sodium hydroxide, washed again with distilled water and dried, washed with methylated spirit and dried, and finally relubricated. The whole apparatus was in a double-walled thermostat room. In the case of the later experiments the electric stirrer was removed from the rectangular tank containing the horizontal capillary tube, in order to eliminate the possibility of vibrations affecting the results.

With these changes the experimental work proceeded as with the stronger manometric liquids. The thermostatic conditions of the room were relied upon to maintain the apparatus at a reasonably constant temperature, and to keep an even distribution of temperature throughout. As an example, during the experiment of March 26, the average room-temperature varied by 0·4° C., and the temperature of the tank containing the index tube varied by 0·15° C. The temperature of the water jacket surrounding the heating section of the apparatus varied by 0·07° C.

§ 15. SUMMARY OF RESULTS

Density difference (gm./cm³)	Date, 1931	Measured manometer difference a (cm.)	Calculated manometer difference b (cm.)	Difference $a - b$ (cm.)	Average difference	Average difference %	a (dyne/cm²)	b (dyne/cm²)	$a - b$ (dyne/cm²)	Di enc
0·0005283	July 11	38·92	39·14	− 0·22	− 0·3	− 0·78	20·17	20·29	− 0·12	−
	July 19	37·59	37·54	+ 0·05			19·47	19·45	+ 0·02	+
	July 21	37·86	38·59	− 0·73			19·62	20·00	− 0·38	−
0·0002112	July 25	51·93	52·47	− 0·54	+ 0·013	+ 0·025	10·76	10·87	− 0·11	−
	July 28	51·34	51·77	− 0·43			10·64	10·73	− 0·09	−
	July 31	53·74	53·35	+ 0·39			11·13	11·05	+ 0·08	+
	Aug. 1	52·86	52·77	+ 0·09			10·95	10·93	+ 0·02	+
	Aug. 4	53·00	52·77	+ 0·23			10·98	10·93	+ 0·05	+
	Aug. 8	53·24	52·90	+ 0·34			11·04	10·95	+ 0·09	+
0·0001678	Aug. 15	47·91	48·48	− 0·57	+ 0·00	+ 0·00	7·89	7·98	− 0·09	−
	Sept. 12	48·83	48·17	+ 0·66			8·04	7·93	+ 0·11	+
	Sept. 19	48·43	48·52	− 0·09			7·97	7·99	− 0·02	
0·0001049	1932				− 0·34	− 0·65				
	Apr. 10	50·77	51·84	− 1·07			5·23	5·33	− 0·10	−
	Apr. 16	51·53	52·34	− 0·81			5·30	5·39	− 0·09	−
	Apr. 23	53·01	53·27	− 0·26			5·46	5·48	− 0·02	−
	Apr. 30	53·59	53·25	+ 0·34			5·52	5·48	+ 0·04	+
	May 7	52·21	52·13	+ 0·08			5·37	5·31	+ 0·06	+
0·00005245	Feb. 6	49·17	49·51	− 0·34	− 0·10	− 0·19	2·53	2·55	− 0·02	−
	Feb. 13	54·35	55·67	− 1·32			2·80	2·86	− 0·06	−
	Mar. 26	52·78	52·82	− 0·04			2·72	2·72	− 0·00	−
	Mar. 30	52·39	52·49	− 0·10			2·70	2·70	− 0·00	−
	May 15	54·68	53·55	+ 1·13			2·81	2·76	+ 0·05	+
	May 21	52·72	52·67	+ 0·05			2·71	2·71	+ 0·00	+
						Average − 0·30				Av −

§ 16. TESTS OF ACCURACY

The index tube was separated from the rest of the apparatus and a fine capillary tube was attached to one end, while the other end was connected to a head of water. By preliminary experiments the head of water and the fineness of the capillary tube were so adjusted that the flows of water through the capillary tube and index tube were approximately those of the slow-flow experiments. An index was introduced into the index tube, and its movement was measured by the centre-of-gravity method already explained in § 12 of this paper. The corresponding flow of water through the index tube was measured by dipping the free end of the capillary tubing into a weighed beaker of water, whose surface was covered with medicinal paraffin oil. The increase in the weight of the beaker and its contents gave the flow of water through the index tube in grams. From the linear movement

of the index obtained by the method quoted above, the volume flow in cubic centimetres was obtained from the calibration graph. The flow as given by the movement of the index should, if the method be right, equal that given by the weighing.

The following results show that the measurements of the linear flow as described in this paper are correct to a fraction of 1 per cent.

periments ...	1	2	3	4	5	6	7	8	9	10
ure heads)	30·0	30·0	27·0	24·5	20·5	24·5	14·3	15·0	6·5	9·0
ır flow (cm.)	96·29	61·95	80·0	88·85	88·5	92·45	88·52	90·0	83·95	81·6
(min.)	261	216	320	346	390	420	540	590	1300	1365
d (cm./hour)	22·14	17·2	15·0	15·5	12·9	13·2	9·84	9·14	3·9	3·59
$^{-6}$ × cm^3/min.)	6330	5139	4279	4422	3879	3788	2805	2625	1104	1023
x flow *a* (gm.)	1·650	1·093	1·374	1·525	1·515	1·584	1·515	1·544	1·439	1·399
by weighing gm.)	1·652	1·110	1·368	1·530	1·513	1·591	1·507	1·549	1·434	1·396
entage differe between *a* *b*	− 0·12	− 0·60	+ 0·40	− 0·30	+ 0·17	− 0·44	+ 0·50	− 0·32	+ 0·30	+ 0·22

The average percentage difference between *a* and *b* is 0·34 per cent.

It ought to be mentioned that the taps were far from ideal: the bores of the taps were far from cylindrical in shape. In fact they were of conical shape near the barrel. The index had to travel through the wide spaces at the end of the bore and when it had emerged from the tube between the taps *C* and *D*, figure 2, it was very unsymmetrical, and was longer than it would have been if the taps had been perfect. Moreover, shortly after emerging from the tap, the index had to pass through an enlargement of the bore made in the sealing together of the parts of the apparatus. This still further increased the dissymmetry and the length of the index.

In order to test the accuracy with which the manometer could be read, experiments were made with a silica apparatus constructed according to the design suggested in figure 8. *A* is an ordinary tap, *B* and *C* are three-way taps of the same type as those used in the manometer. The length of the apparatus is about 30 cm., that is, the distance round the circuit is about 60 cm., and the bore of the tube is about 0·2 cm. The part of the apparatus below *B* and *C* was filled with a uranine solution and that above *B* with distilled water. It was hoped that on arranging the taps *B* and *C* so that a vertical flow could take place, the difference in level between the ends of the columns of uranine solution would gradually become zero and remain zero. This was the case with the comparatively strong solution of uranine, viz. 0·000250 gm./cm^3. The difference did become zero and remained at zero; but with very feeble solutions the results were of an unexpected character.

Figure 8.

The rate of movement of the ends of the columns in this latter case was not in accordance with the rate of movement as calculated from the dimensions of the apparatus, the viscosity of water, and the density of the uranine; and moreover the difference of level did not remain at zero after reaching zero, for when the difference of level was zero the columns were in movement, and the extremity of the left-hand column later became higher than that of the right, once by 2 cm. Then there was a slow reverse movement, and after two or three days the difference of level became zero.

The experiments suggest that when the feeble solutions were used in the manometer described in this paper, it would have been better to have had an interval of two or three days after filling the apparatus before making comparison between the pressure as deduced from the flow and that given by the manometer. In practice the interval was generally from 16 to 20 hours.

If it is possible to make further experiments, the hypothesis will be made that the anomalous results of the feeble solutions were due to small particles suspended in the water, and that these particles gradually subsided, or deposited themselves on the walls of the silica tube.

The apparatus was made with the assistance of a grant from the Waller Research Fund.

§ 17. ACKNOWLEDGMENT

Thanks are due to Dr Constance H. Griffiths, a fellow research student, who gave valuable help by her general interest in the progress of the work, and particularly by her assistance in the careful density difference determinations.

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AN APPLICATION OF A NEW METHOD, DUE TO PROFESSOR ALBERT GRIFFITHS, OF DETERMINING A SMALL CHANGE IN THE DENSITY OF A LIQUID

By P. C. VINCENT, M.Sc., Research Student, Birkbeck College

Communicated by Prof. Albert Griffiths, April 24, 1933

ABSTRACT. The paper describes a manometer method for determining changes in the density of water due to prolonged contact with glass.

THIS paper is a continuation of a previous paper* and describes a rough measurement of the change in density of water which has been standing in glass tubes for days. It describes experiments which (*a*) support the hypothesis that the solution of the glass by water with a consequent increase in the density was responsible for the remarkable results obtained with the manometer made of glass tubing; (*b*) show that the density of water kept in a silica tube does not change appreciably in the course of weeks; and (*c*) enable the changes in density of samples of water which have been kept in contact with glass for various periods to be obtained.

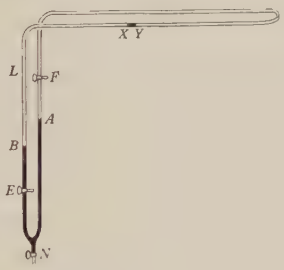

Figure 1.

For simplicity of explanation consider the apparatus modified as in figure 1. If the closed circuit be filled with liquid of uniform density, there will be no movement of the liquid; but if a denser liquid be introduced as indicated in the figure, and if the level A of the denser liquid be higher than the level B, a movement of the index XY will take place from left to right. If on the other hand B be at a higher level than A, the movement will be in the opposite direction.

By the virtual elimination of the parts $HOAPJ$ of figure 2 of the prior paper, the apparatus depicted in figure 1 is obtained. In practice it was found advisable

* Page 808 of this issue.

to introduce a length of indiarubber tubing provided with a screw clip into *HO* and also to introduce a similar length of tube into the part *PJ*.

Experiments A. (1) After the apparatus had been filled with pure water and had settled down, a new sample of pure water was introduced into the space *FNE*. As was expected there was no movement of the index. (2) Four times, water which had been in glass tubes of diameter approximately 0·2 cm. for periods varying from 4 to 29 days was introduced into *FNE*. In each case the index moved in the direction expected. (3) Twice, water which had been in glass tubes for periods of 8 and 31 days respectively was introduced into the tube at the three-way tap *E*, figure 1, so as to occupy the part of the tube *EL*. The index now moved in the opposite direction, i.e. in the direction expected. The details of the method employed are not given here.

Experiments B. (1) Water which had been left in a silica tube of diameter 0·2 cm. for 27 days was introduced into the space *FNE*. There was a negligible movement of the index and then it remained stationary. (2) Water which had been in the silica tube for 31 days caused a negligible movement of the index in the opposite direction and again came to rest.

Consider the case in which the water from a glass tube has been introduced into the portion of the tube between *F* and *E*. At a given moment the flow is started.

t Let t be the time measured from the moment of starting;

v v the volume flow in time t;

z z the coefficient of viscosity of the water;

V V half the volume in the manometer between the taps *F* and *E*, that is the total volume flow;

A A the area of the cross-section of the manometer tube.

R The circuit is not of uniform bore; let R denote the value of $(L_1 r_1^4 + L_2 r_2^4)$, where the letters have the obvious meaning.

ρ Let ρ indicate the difference in density between water that has been in the glass tube and pure water.

Then, as is well known in the case of such a circuit, the relation between v and t involves an exponential function of the time, thus

$$v = V(1 - e^{-\rho\lambda t}),$$

λ where λ is a constant. The value of λ in this particular case is $\frac{\pi g}{4ARz}$.

Let $f(v)$ be equal to $\frac{1}{\lambda} \log_e \frac{V}{V - v}$, then it can easily be shown that

$$\rho = f(v)/t.$$

If t be plotted as abscissa and $f(v)$ as ordinate, an approximation to a straight line is obtained, and $\rho = \tan\theta$, where θ is the angle the straight line makes with the abscissa.

Experiments C. (1) The graph, figure 2, shows the result obtained in the experiment of June 8, 1930, when the manometer water had been in the glass tube

for 29 days, and where $\rho = 0{\cdot}00013$ gm./cm.^{3} (2) In a second experiment, where the water had been in the glass tube for 7 days only, $\rho = 0{\cdot}000022$ gm./cm.^{3} (3) In a third experiment, where the water had been in the glass tube for 24 days, $\rho = 0{\cdot}000054$ gm./cm.^{3}

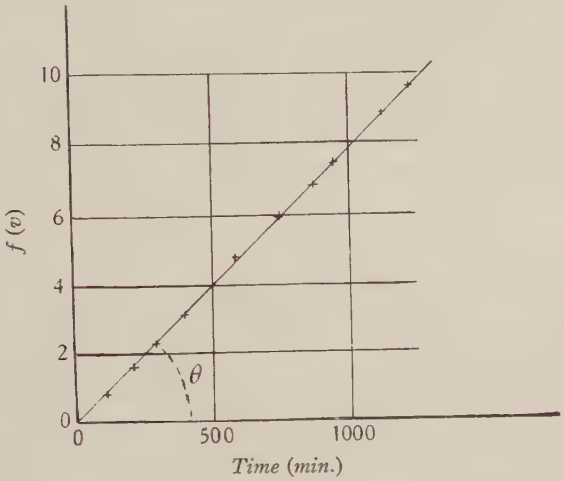

Figure 2.

To save expense, part of the apparatus used for the manometer experiments described in the previous paper was employed. It might be an improvement to increase the diameter of the vertical tubes. In this case the speed of the index would not diminish considerably during the course of an experiment. If one knew the difference between the density of a standard weak solution and that of water, it would not be necessary to know the exact dimensions of the apparatus. The difference in density would be inversely proportional to the time taken for the index to move through a given range.

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SOME COMPLEMENTARY COLOUR RELATIONS

By ERIK GENBERG, Norrköping, Sweden

Communicated by J. Guild, September 12, 1933

ABSTRACT. The author has determined pairs of wave-lengths which are complementary with respect to equi-energy radiation taken as white. The energy and luminosity of one of the complementaries for unit luminosity of the white are given.

§ 1

A pair of stimuli which, when combined in a certain proportion, are able to match white are known as complementary stimuli. These pairs can be determined geometrically from the spectral curve on the colour triangle or algebraically from the C.I.E. colorimetric standards or the corresponding values in another system. In both cases the coordinates of the white must be known, and it is impossible to deal with complementaries except with regard to a certain selected white.

When we seek to define a standard white, we find that there is nothing to make us prefer one blend of spectral energies to another. A unique white does not exist. Daylight, which we commonly consider as producing a colourless sensation, varies considerably in its properties both in different parts of the world and at different seasons, as well as at different times of the day. The daylight therefore is not a defined blend of spectral energies and cannot be used as an adequate definition of a white light.

The only way to find a standard white is to discard subjective criteria of whiteness and choose a radiation with certain physical properties. The simplest of these radiations is the equi-energy radiation, and in the present paper this hypothetical blend is to be considered as the white, to which the complementary pairs are to be referred.

It must be noted that the sensation produced by an equi-energy radiation does not differ very much from those produced by sources which we commonly consider as white, and therefore no serious objections can be raised against the above choice on the ground that it does not correspond to subjective white.

We can imagine both real and unreal complementaries, but of greatest interest are the complementary relations for the real stimuli of maximum saturation, i.e. the spectral stimuli and the stimuli which lie on the straight line joining the two ends of the spectral curve, i.e. the most saturated purple colours. It is a well-known fact that the spectral stimuli in the middle region of the spectrum have no spectral complementaries, so in order to get a definition applicable throughout the whole spectrum, J. Guild* has proposed to term these pairs *extreme* complementaries.

* In a private letter to the author.

We denote a trichromatic unit of white and two complementary stimuli by W, A, and B. Their unit equations we denote as follows: W, A, B

$$\left.\begin{aligned} W &= x_0 X + y_0 Y + z_0 Z \\ A &= x_1 X + y_1 Y + z_1 Z \\ B &= x_2 X + y_2 Y + z_2 Z \end{aligned}\right\} \quad \ldots\ldots(1). \qquad \begin{matrix} X, Y, Z \\ x, y, z \\ 1, 2 \end{matrix}$$

In the colour triangle these three colours must lie on the same straight line. As the condition for complementarity we therefore obtain

$$\begin{vmatrix} x_0 & y_0 & z_0 \\ x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \end{vmatrix} = 0 \qquad \ldots\ldots(2).$$

For a system where the white lies in the centre of the colour triangle we get

$$\begin{vmatrix} 1 & 1 & 1 \\ x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \end{vmatrix} = 0 \qquad \ldots\ldots(3)$$

and

$$x_1 \frac{3y_2 - 1}{y_2 - x_2} - y_1 \frac{3x_2 - 1}{y_2 - x_2} = 1 \qquad \ldots\ldots(3\,a).$$

From this equation we can derive the spectral complementaries shown in the table. For the spectral stimuli, which have no spectral complementaries, the

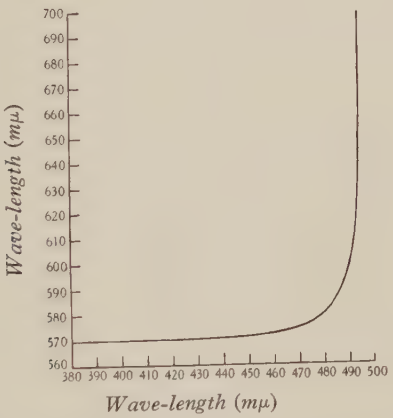

Figure 1. The spectral complementaries in regard to equi-energy-white.

extreme complementaries must lie on the straight line joining the two ends of the spectral curve. We denote a trichromatic unit of the two end colours by M and N, and their unit equations as follows: M, N

$$\left.\begin{aligned} M &= x' X + y' Y + z' Z \\ N &= x'' X + y'' Y + z'' Z \end{aligned}\right\} \quad \ldots\ldots(4). \qquad ', ''$$

If the colour A lies on this line, its co-ordinates must satisfy the equation

$$\begin{vmatrix} x_1 & y_1 & z_1 \\ x' & y' & z' \\ x'' & y'' & z'' \end{vmatrix} = \begin{vmatrix} x_1 & y_1 & 1 \\ x' & y' & 1 \\ x'' & y'' & 1 \end{vmatrix} = 0 \qquad \text{.....(5),}$$

$$y_1 - y' = \frac{y'' - y'}{x'' - x'}(x_1 - x') \qquad \text{.....(5 a).}$$

In the C.I.E. system we obtain

$$\left.\begin{array}{ll} \lambda' = 700 & \lambda'' = 380 \\ x' = 0{\cdot}7347 & x'' = 0{\cdot}1741 \\ y' = 0{\cdot}2653 & y'' = 0{\cdot}0050 \end{array}\right| \qquad \text{.....(6),}$$

(5, 6) $y_1 = 0{\cdot}4643 \qquad x_1 - 0{\cdot}0758$ .....(7).

We now derive

(3, 7) $$x_1 = \frac{(y_2 - 1{\cdot}2274)(x_2 + 0{\cdot}0758)}{(3y_2 - 1{\cdot}3929)(x_2 - 0{\cdot}5357)} \qquad \text{.....(8).}$$

From the equations (7) and (8) we can calculate the co-ordinates for the extreme complementaries which are non-spectral stimuli. These also are shown in the table.

§ 2

We shall now calculate the quantities of the complementaries which are necessary to match the white, and therefore we transform its co-ordinates to the system ABC,

C where C is an arbitrary colour with the unit equation

3 $$C = x_3 X + y_3 Y + z_3 Z \qquad \text{.....(9).}$$

A and B are defined above. The new unit equation for white we write

a, b, c $$W = aA + bB + cC \qquad \text{.....(10)}$$

and obtain

$$\left.\begin{array}{l} a = \frac{1}{3}\frac{D_1}{D} \\ b = \frac{1}{3}\frac{D_2}{D} \\ c = \frac{1}{3}\frac{D_3}{D} \end{array}\right| \qquad \text{.....(11),}$$

where

D_1 $$D_1 = \begin{vmatrix} 1 & 1 & 1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} \text{ etc}$$

and

D $$D = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix}.$$

In regard to the condition for complementarity (3) we obtain

$$\left.\begin{aligned} a &= \frac{1}{3}\frac{1-3x_2}{x_1-x_2} \\ b &= \frac{1}{3}\frac{1-3x_1}{x_2-x_1} \\ c &= 0 \end{aligned}\right\} \qquad \text{.....(11 a)},$$

$$a+b=1 \qquad \text{.....(12)}.$$

The luminosities we denote by L and obtain

$$L_W = aL_A + bL_B \qquad \text{.....(13)},$$

$$\left.\begin{aligned} L_A &= x_1L_x + y_1L_y + z_1L_z \\ L_B &= x_2L_x + y_2L_y + z_2L_z \end{aligned}\right\} \qquad \text{.....(14)},$$

(11 *a*, 13, 14)

$$L_W = \tfrac{1}{3}(L_x + L_y + L_z) \qquad \text{.....(13 a)}.$$

The luminosity of that quantity of the colour A, which with its complementary colour B matches a white colour of unit luminosity, we denote by L_a and get

$$L_a = \frac{aL_A}{L_W} = \frac{1-3x_2}{x_1-x_2}\frac{L_A}{L_x+L_y+L_z} \qquad \text{.....(15)}.$$

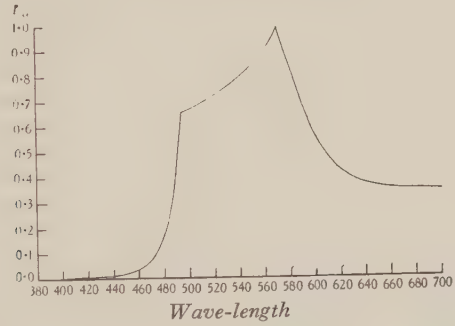

Figure 2. Luminosity values for spectral stimuli matching equi-energy white of unit luminosity with their extreme complementaries.

In the C.I.E. system

$$\left.\begin{aligned} L_x &= 0 \\ L_y &= 1 \\ L_z &= 0 \end{aligned}\right\} \qquad \text{.....(16)},$$

(15, 16)

$$L_a = y_1\frac{1-3x_2}{x_1-x_2} \qquad \text{.....(15 a)}.$$

If the standard visibility function is denoted by V, the energy which corresponds to the luminosity L_a is expressed, in arbitrary units, by

$$E_a = L_a/V_A \qquad \text{.....(17)}.$$

From equations (15 *a*) and (17) the luminosity and energy values shown in the table are calculated.

Table. The complementary colours which for a 1931 C.I.E.-standard observer are chromatically equivalent to an equi-energy radiation of unit luminosity

λ_a	L_a	E_a		λ_b	
700	0·344	84		493·9	
690	0·345	42		493·9	
680	0·346	20·4		493·9	
670	0·348	10·9		493·8	
660	0·352	5·77		493·7	
650	0·359	5·36		493·6	
640	0·371	2·12		493·5	
630	0·391	1·47		493·2	
620	0·421	1·10		492·6	
610	0·472	0·94		491·7	
600	0·553	0·88		490·0	
590	0·675	0·89		486·8	
580	0·836	0·96		479·6	
570	0·992	1·04		427·3	
			x	y	z
560	0·903	0·91	0·2963	0·0618	0·6419
550	0·840	0·84	0·3549	0·0890	0·5561
540	0·796	0·83	0·3896	0·1051	0·5053
530	0·759	0·88	0·4151	0·1169	0·4680
520	0·727	1·02	0·4395	0·1283	0·4322
510	0·699	1·39	0·4771	0·1457	0·3772
500	0·673	2·08	0·5656	0·1868	0·2476
				λ_b	
490	0·447	4·05		600·0	
480	0·171	2·32		580·4	
470	0·071	1·46		574·8	
460	0·036	1·12		572·4	
450	0·021	1·06		571·3	
440	0·013	1·08		570·5	
430	0·008	1·36		570·1	
420	0·006	2·92		569·9	
410	0·006	9·1		569·8	
400	0·006	27·4		569·7	
390	0·006	93·0		569·7	
380	0·006	286		569·7	

OBITUARY NOTICES

EDWIN EDSER, A.R.C.Sc., F.Inst.P.

Edwin Edser, who died on August 17, 1932, will be remembered as an inspiring colleague by many who at some time had the privilege of working with him, and as a clear exponent in many branches of physics by the much larger body who used his text-books. He always brought original ideas to the solution of any problem, and although he was best known as an experimentalist, he was no mean mathematician. In his text-books he always avoided the use of the differential and integral calculus but, as he said, a use of the calculus often evades the real understanding of the problem, and anyone familiar with the methods of the calculus can abbreviate the proofs he gave by employing the symbolic method.

Edser completed his days as a student at the Royal College of Science in 1892 by taking the Associateship of that College, but at this early date he exhibited his originality and experimental ability by devising in conjunction with Herbert Stansfield a portable instrument for measuring magnetic fields* which shows a care in the detail of construction not always attained. From 1892 to 1895 Edser was a demonstrator in the physical laboratory of the Royal College of Science, and during this time his chief interest lay in constructing an efficient form of Michelson's interferometer with the view of measuring the effect of the motion of water upon the velocity of light propagated in the direction of movement of the water. In conjunction with Prof. A. W. Rücker he showed that the combination tones produced by two sounding bodies had an objective existence†. Attaching one of the mirrors of Michelson's interferometer to a fork of pitch equal to the required combination tone, he showed by the disappearance of the fringes that the fork was resounding and consequently that the tone had an objective existence and was not a subjective effect.

From 1895 to 1903 Edser was in charge of the teaching of physics in the South-Western Polytechnic, Chelsea, and during this time he published, with C. P. Butler, the simple method of calibrating prismatic spectra which still goes by his name‡. Two reflecting surfaces at a small angle, such as two pieces of plate glass, are placed in front of the slit of the spectroscope. The spectrum is then crossed by a number of light and dark hands which form a wave-length scale, so that if any two lines of known wave-length are present, the other lines can be determined to within 0·4 tenth-metre. At this time too he found one of those gaps in classical theory which, as he said, he had always looked for but never hoped to find. This is indicated in the title of his paper to the Royal Society "An extension of Maxwell's electromagnetic theory of light to include dispersion, metallic

* *Phil. Mag.* **34**, 186 (1892).
‡ *Phil. Mag.* **46**, 207 (1898).
† *Proc. Phys. Soc.* **13**, 412 (1895).

reflection and allied phenomena"*. Treating a dielectric as consisting, like an electrolyte, of molecules having two oppositely charged atoms, we have in the simplest case, in a field P,

$$P(1 + 4\pi M) = 4\pi D,$$

where $1 + 4\pi M$ represents the dielectric constant. Maxwell's first equation is unchanged, but the second equation is modified by adding $\Sigma q v_x$ to the displacement current, where q is the atomic charge and v_x the velocity of that charge. Subsidiary equations for atomic vibrations (rotational and separational) are given, and finally

$$\mu^2 = \mu_\alpha + \frac{c'\lambda^2}{\lambda^2 - \lambda_1^2} + \frac{c''\lambda_2^2}{\lambda^2 - \lambda_2^2},$$

which is the most general form of Ketteler's dispersion formula. Double refraction in uniaxal crystals is discussed, an extension is made by introducing a viscous term, and the ordinary laws of metallic reflection as given by Cauchy are deduced. His treatment is an improvement on Helmholtz's theory, as a more definite physical significance is given to the constants introduced.

From 1903 to 1914 Edser was Head of the Department of Physics at the Goldsmith's College, and took considerable part in the academic work of the University of London. In 1914 he published a paper on "The reflexion of electromagnetic waves at the surface of a moving mirror"†. By showing that a unit charge in the conducting mirror is subject not only to the electric fields of the incident and reflected waves but also to a force in their magnetic fields due to its own motion with the mirror, he proved that the amplitude of the reflected wave is not the same as that of the incident wave. The case of oblique incidence also was treated.

From 1915 Edser devoted himself to the work of Minerals Separation, Ltd. and here his interest in the subject of surface tension proved of immense value. His two articles in the *Reports on Colloidal Chemistry* of the British Association are of importance in the metallurgical processes concerned, but above all make a valuable and fascinating addition to the literature on the subject. The first article on "Molecular attraction and the physical properties of liquids"‡ comprises in the first place a review of the possible laws of attraction which account for the facts of surface tension, intrinsic pressure, and cohesion, giving in historical order the methods of Laplace, Rayleigh and others. Then, assuming that attraction $\propto r^{-n}$, he calculates the cohesion by two independent methods: first directly from the definition of cohesion by integration, across an imaginary plane, of the forces due to the individual molecules on opposite sides of it; and secondly from the expression for cohesion extracted from the virial equation of Clausius. The two methods give identical results. n must be greater than 4 for cohesion to exist at all. Surface tension is then calculated by Gauss's method and it becomes obvious that for surface tension to exist at all n must be greater than 5. From the surface tension of very small bubbles and drops it appears that n must be greater than 7.

* *Proc. R.S.* **63**, 91 (1898).

† *Phil. Mag.* **28**, 508 (1914).

‡ *Fourth Report Coll. Chem. Brit. Assoc.* p. 40 (1922).

Probably $n = 8$. No assumptions are made as to the structure of the molecule. Two further conclusions are aimed at, namely that the energy of surface tension exists to the extent of 94 per cent in a layer one molecule thick, and that at a depth equal to a molecular diameter the intrinsic pressure is 8·5 per cent less than the maximum value in the interior of the liquid. Tables of surface density calculated from latent heats for 65 substances show sufficient agreement with the experimental values to bear out the validity of the work, and a similar agreement exists in the case of 84 substances in which it is calculated from the density and thermal expansibility. The remaining paper* on "The concentration of minerals by flotation" describes the flotation of heavy bodies on liquids and its applications in separating floatable materials such as galena and blende from non-floatable materials such as quartz. A heavy body which floats upon a liquid is supported by the surface tension of the liquid and by the hydrostatic pressure of the liquid below it; the former predominates for small bodies and the latter for large ones. The adhesion to bubbles in a froth has a similar cause and the methods of producing flocculation and deflocculation are described and discussed. Flocculation is explained in terms of the angle of contact between the air-liquid surface and the liquid-solid interface owing to the repulsion of the water from between the particles and the consequent moving together of the particles as though attraction existed. The particles that can be flocculated are exactly those that can float on a liquid less dense than themselves.

Every branch of physics touched by Edser was elucidated by his active mind, and although his work was not all well known it was all of high intrinsic merit.

S. G. STARLING

* *Fourth Report Coll. Chem. Brit. Assoc.* p. 263.

SIR RICHARD THRELFALL

With the passing of Sir Richard Threlfall in July 1932 a gap was left in the ranks of men of science which, in these days of specialization, it will be hard to fill, for Sir Richard was many-sided in his interests and yet no dilettante. He spoke with knowledge and authority among chemists, physicists, and mechanical or electrical engineers, and was keenly interested in horticulture and entomology. Once his interest in a problem was aroused, no matter what the subject, he would attack it scientifically, and continue the attack from all sides until he could see clearly the way to a solution. By training and inclination he was a physicist, and spoke of himself as a "chemist by adoption": nevertheless it was to Sir Richard Threlfall that the Society of Chemical Industry in 1929 awarded its medal—the blue riband of the profession of applied chemistry.

He used to relate how, as a boy, he learnt all the tricks of the trade that the village blacksmith could teach him, and spent his pocket-money on materials for experiments, making most of his own apparatus. To the end of his life he preferred the old type of Bunsen burner to the more modern adaptations of it. His book *Laboratory Arts* (Macmillan), first published in 1898, was no scissors-and-paste compilation; it was obviously written by one who had himself used the methods there described, many of which were original.

Of the twenty or so various researches, the results of which he published during the period 1886–1899, many have a distinct bearing on pure chemistry. From his early association with Prof. J. J. Thomson in researches on the effect produced by the passage of electric discharge through pure nitrogen and on the production of ozone he was led to study the electrical properties of pure substances; in the *Philosophical Magazine* for 1893 he describes the preparation of pure nitrogen and attempts to condense it, and in the *Philosophical Transactions* for 1894 he describes the electrical properties of pure sulphur.

It was during his residence in Sydney (1886–1899) as Professor of Physics at the University that Threlfall became interested in the study of fuels from the chemical as well as the physical point of view, and he was appointed President of the First and Second New South Wales Royal Commission on the spontaneous combustion of coal cargoes. His interest in fuel problems and the economic generation of power found scope at a later date when in 1899 he joined the firm of Messrs Albright and Wilson, Ltd., of Oldbury, Birmingham. Here he devoted himself to the direction of researches bearing on the application of engineering, and particularly electrical engineering, to chemical manufacture. The generation of producer gas and its distribution early claimed his attention, and formed the subject of a paper read to the Society of Chemical Industry in 1907. The methods then used for the metering of large volumes of producer gas were far from satis-

factory, on account of interference due to deposition of tar in the mains. Threlfall selected the Pitot-tube method as the most suitable and, after a careful study of the factors involved, incorporated it in a continuous recording instrument, which he described before the Institution of Mechanical Engineers in 1904.

Sir Richard Threlfall's intimate knowledge not only of fuel problems but also of the requirements of industries depending upon the economic utilization of our fuel supplies led to his appointment as Chairman of the Fuel Research Board in succession to Sir George Beilby.

As Technical Director of Messrs Albright and Wilson, Ltd., which post he held until shortly before his death, he undertook the investigation of electrochemical methods for the commercial production more particularly of potassium chlorate, ammonium persulphate and electrolytic zinc. Many of his noteworthy achievements in this connection are necessarily as yet unpublished. They are triumphs of chemical engineering. As early as 1894, when resident in Australia, he had been interested in the zinc workings at Broken Hill and had recognized the potentialities of pure electrolytic zinc, but it was not until nearly fifteen years later that the commercial production of pure zinc became attractive. Threlfall courageously decided to manufacture from fused zinc chloride. The economic production of zinc chloride and its dehydration on a large scale in such a way as to avoid the formation of the oxychloride had not hitherto been achieved. A full description of the process, together with the still more original methods used for electrolysis of the fused chloride, is to be found in the *Transactions of the Society of Chemical Industry* for 1929. On reading the account of this work one is struck with the tenacity and perseverance shown in overcoming almost insuperable difficulties in the use of unusual materials of construction. The more difficult the problem experimentally, the more it appealed to Threlfall—his interest was "where the cackle ends and where the 'osses begin."

During the War his services were enlisted on the Trench Warfare Committee, and subsequently on the Board of Invention and Research and the Chemical Warfare Committee. In this capacity he was instrumental in initiating many lines of activity. He was early recognized as an authority on the production of smoke screens and bombs. Jointly with Sir William Ramsay he was the first to explore the possibility of developing supplies of helium for use in airships within the Empire, and in his own laboratory he carried out many experiments on the production and safe handling of hydrogen.

As Chairman of the Chemistry Co-ordination Research Board, Threlfall saw clearly the need and scope for a national research institution, and chemists owe to him more than to any other the foundation of the Chemical Research Laboratories at Teddington—a fitting monument to a life spent in the service of technical chemistry.

G. KING

SIR RICHARD THRELFALL, the experimentalist

Sir Richard Threlfall was essentially a skilled experimentalist ready to embark on any difficult investigation that interested him, and it may be said that the more difficult it was the more he revelled in it. In all he did his strong personality asserted itself.

The variety of laboratory operations which he had practised is illustrated in his book *On Laboratory Arts* (1898) which, like Shenstone's book on glass-blowing, bears on every page clear evidence of personal attention to detail. Detail is hardly the word; I mean the minutest detail in an operation which is important in facilitating its practice or in ensuring success. Those who are not themselves skilled experimenters, that is those who do not do things but merely talk or write or calculate about things done by others, may not appreciate how much there is in such detail. Threlfall in his book emphasized this, for he said he had not, except where he had specifically stated the contrary, described any operation which he had not practised himself, and he might have added "in which he was not also an adept."

His manipulative skill was great and the fact that he had lost several fingers from too incautious experiment with nitro-explosives did not deter him from his beloved laboratory pursuits.

It seems to me a sad reflection that his book on laboratory arts should so long have remained out of print. A new edition was badly needed and in his last years he was, it seemed to me, rather half-heartedly preparing for a new edition. It is to be hoped that someone who is equally skilled and who is familiar with the multitude of modern laboratory operations at first hand may be induced to carry on where Threlfall left off, and complete a new edition.

Threlfall's exceptional personality must have been a surprise to the University authorities at Sydney when he first arrived as the newly appointed professor of physics. He found they had nothing at all in the way of laboratory or equipment. No doubt there was a blackboard. Threlfall demanded instantly that tools and apparatus of which he presented a list should be provided. This was an uncontemplated, and no doubt some thought it an unnecessary, expense, and when they seemed disinclined to meet his wishes in the matter he answered "I am going back to England by the next ship." He got all he wanted. I regret that I cannot refer to any document to confirm this story. It is just as I remember it from his own lips. It may in detail be not exactly right but substantially it is.

From his book, of which I am glad to own a presentation copy, it will be seen how thoroughly he pursued and how far he advanced in a number of difficult laboratory arts. His glass-blowing was quite exceptional for a non-professional, and the casual amateur would do well to notice, merely as one instance of attention to detail, how much trouble and care Threlfall took in cleaning his glass before operating upon it.

It used to be not unusual to find amateurs who make their own telescope mirrors, and some really excellent mirrors have so been made. It is sufficient to mention A. A. Common, who started as an amateur. Threlfall, however, went further and made an acromatic telescope objective and other lenses. This was before the days of the triple objective, so we find the ordinary acromatic pair of flint and crown.

Among the laboratory operations described in detail by Threlfall was one which more particularly interests me, that of making quartz fibres. These attracted much attention in this country when I first showed them in 1887, but I do not remember that anyone here meddled with them until Shenstone, a Master at Clifton College, got interested. Threlfall, however, read about them, and not deterred by the handicap of missing fingers experimented at first unsuccessfully. On reading further accounts he started again and succeeded perfectly. He then found that in describing the perfect elasticity of the fibres I had understated the case and, as he said in the words of the Queen of Sheba, the half had not been told to him. It may be of interest to give what I believe to be the reason for his first want of success, because I experienced this myself for I think two whole days. It is repugnant to anyone who is a glass-blower to try to do any work in the flame, and it must have been as impossible for Threlfall as it was to me to dare to draw the fibres actually in that intensely hot oxyhydrogen flame. I still cannot understand why they do not draw off. Threlfall made use of the extreme perfection of the elasticity to make a gravimeter, but then he found that the fibres had a positive temperature coefficient of rigidity which required very good thermostatic means to counteract it.

In later years Threlfall developed a recording gas calorimeter, and to resist the highly corrosive products of combustion of the Mond gas for which it was made he used pure lead for the combustion chamber. In this I was glad to follow him until I found a better material.

I regret that I am unable to add any observations on his later activities. These have related largely to manufacturing operations, and naturally he did not discuss these outside the works.

C. V. BOYS

REVIEW OF BOOK

Applied X-Rays, by G. C. Clark. 2nd edition. 470 pp. (McGraw-Hill.) 30*s*. net.

This well-known work has won a niche for itself in the literature of the subject. The second edition is considerably larger than the first and the matter is presented in a more logical order. The book is divided into two parts, the first dealing with general physics and the applications of X-rays, and the second with the X-ray analysis of the ultimate structures of materials.

The book has been largely re-written except for some of the material in the earlier portions. The results of the crystal analysis of elements and compounds are brought up to date and valuable tables of the structures of elements and compounds are included. A useful and concise account is given of the structure of alloys and the attempts which are now being made to explain their properties. This is followed by a summary of recent work on the diffraction of X-rays by liquids and amorphous bodies. Completely new chapters have been written on chemical analysis by X-rays, inorganic crystal chemistry (in which the laws of formation of crystals, types of bonding, co-ordination in crystals, etc. are discussed according to recent notions) and the structure of highly polymerized organic substances found in nature.

The author has endeavoured to supply sufficient theoretical framework to elucidate the interpretation of the results obtained by X-ray methods, but the theoretical explanations suffer in general from too much compression. This is especially noticeable in the account of the determination of atomic arrangement from intensity data.

We have noted a few omissions and inaccuracies. The two photographs of single crystals of sapphire on p. 352 are incorrectly described as Laue patterns, and it is a little surprising to find in the section dealing with fibre-structure no indication of any methods other than trial and error, and that no reference is made to the pole-figures of Wever, upon which so much of the best work depends.

The book bears evidence of an attempt to cater for the intelligent inquirer and at the same time to satisfy the experimentalist, and on the whole the attempt is successful. An immense amount of information is contained in it, and it will no doubt continue to be used by those who are interested in the subject of applied X-rays.

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PROCEEDINGS AT THE MEETINGS OF THE PHYSICAL SOCIETY

SESSION 1932–33

Except where the contrary is stated, the meetings were held at the Imperial College of Science and Technology, South Kensington.

October 7, 1932.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Sidney Weintroub and Elsie A. Simmons were elected to Fellowship of the Physical Society.

The President announced that Alan Hunter had been elected to Student Membership of the Society.

A lecture was delivered by Dr J. W. FRENCH, F.Inst.P., on "The manufacture of optical glass." The lecture was illustrated by lantern slides and specimens.

October 21, 1932.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Albert E. Bennett, Thomas Alty, George B. H. Haskard, Alexander Harvey, Jarl A. Wasastjerna, and Frederick Charles Smith were elected to Fellowship of the Physical Society.

The President announced that Marcus Campbell Goodall had been elected to Student Membership of the Society.

The following papers were read:

"New apparatus for rapid spectrophotometry of liquids in the ultra-violet region," by F. TWYMAN, F.R.S.

"An experimental study of electrical discharge in gases at normal temperatures and pressures," by J. D. STEPHENSON, B.Sc., Armstrong College, Newcastle-on-Tyne.

"A new type of pendulum clock," by G. A. TOMLINSON, B.Sc.

"A photographic method of deriving optical constants of the metals," by S. E. WILLIAMS, B.Sc.

November 4, 1932.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Donald Laurence Hodge was elected to Fellowship of the Physical Society.

The President announced that F. A. Watson, Robert Henry Taylor Jesson, and Humphry Montague Smith had been elected to Student Membership of the Society.

The following papers were read:

"A further point of analogy between the equations of the quantum theory and Maxwell's equations," by M. FAHMY, The Egyptian University, Cairo.

"The elastic constants of rocks, with a seismic application," by T. C. RICHARDS, A.R.C.S., B.Sc., D.I.C.

"A common misapprehension of the theory of induced magnetism," by L. R. WILBERFORCE, M.A., Lyon Jones Professor of Physics, The University of Liverpool.

A lecture on "Kinematic supports and clamps" was delivered by Prof. L. R. WILBERFORCE.

November 18, 1932.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Donovan Chilton, Frank Walter Dawe, and Charles Thomson Rees Wilson were elected to Fellowship of the Physical Society.

The following papers were read:

"The measurement of surface tension," by T. C. SUTTON, Research Department, Royal Arsenal, Woolwich.

"A sensitivity-control for the Lindemann electrometer," by L. G. GRIMMETT, B.Sc., Assistant Physicist, Westminster Hospital, London.

"An investigation into the flow of air in pipes," by B. LLOYD-EVANS, M.Sc. (Eng.), M.I.Mech.E., and S. S. WATTS, B.Sc. (Eng.), University College, London.

"Vibrations produced in bodies by contact with solid carbon dioxide," by MARY D. WALLER, B.Sc.

The last paper was illustrated with a demonstration.

December 2, 1932.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Thomas Smithies Taylor was elected to Fellowship of the Physical Society.

The President announced that E. D. Eyles and James Harvey Nelson had been admitted to Student Membership of the Society.

The following papers were read:

"Time-marking a cathode-ray oscillogram," by LEWIS F. RICHARDSON, F.R.S.

"The generation and reception of wireless signals of short duration," by J. F. HERD, A.M.I.E.E., Radio Research Station, Slough.

"A comparison of the frequency-change and group-retardation methods of measuring ionized-layer equivalent heights," by R. NAISMITH, A.M.I.E.E.

"The influence of atmospheric suspensoids upon the earth's electric field, as indicated by observations at Kew Observatory," by H. L. WRIGHT, M.A.

December 16, 1932.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Charles T. Archer and Nelson King Johnson were elected to Fellowship of the Physical Society.

The President announced that G. F. Adams, F. Blythem, Ronald W. A. Buswell, William Douglas Bradley, Walter J. C. Chapple, Ronald Walter Douglas and D. P. McKeon were elected to Student Membership of the Society.

The following papers were read:

"A method for the determination of the specific heats of liquids, and a determination of the specific heats of aniline and benzene over the approximate range 20° to 50° C.," by ALLAN FERGUSON, M.A., D.Sc., F.Inst.P., and J. T. MILLER, B.Sc.

"The ionosphere as a doubly refracting medium," by Prof. E. V. APPLETON, F.R.S., and G. BUILDER, B.Sc., King's College, London.

"The Appleton-Hartree formula and dispersion curves for the propagation of electromagnetic waves through an ionized medium in the presence of an external magnetic field. Part 1: Curves for zero absorption," by M. TAYLOR, M.A., Ph.D.

"A new apparatus for the measurement of the earth's magnetic field," by L. F. BATES, Ph.D., F.Inst.P., Reader in Physics, University College, London.

"The flow of liquid suspensions," by E. G. RICHARDSON, B.A., Ph.D., D.Sc., and E. TYLER, D.Sc., F.Inst.P.

"A model to illustrate the motion of a diatomic rotator with two degrees of freedon," by LEWIS SIMONS, D.Sc., F.Inst.P., and E. H. SMART, M.A., Birkbeck College, London.

January 3, 4 *and* 5, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

The twenty-third Annual Exhibition of scientific instruments and apparatus was held at the Imperial College of Science and Technology.

The following discourses were delivered at the Exhibition:

January 3. "Surface tension and its measurement," by ALLAN FERGUSON, M.A., D.Sc., F.Inst.P.

January 4. "Cathode ray oscillography," by R. A. WATSON WATT, B.Sc., A.M.I.E.E., F.Inst.P.

January 5. "Time measurement: old and new," by F. HOPE-JONES, M.I.E.E., F.R.A.S.

January 20, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Charles William Oatley was elected to Fellowship of the Physical Society.

The President announced that Abraham Isidore Vangeen and Herbert James Harold Starks had been elected to Student Membership of the Society.

The following papers were read:

"Notes on the method of least squares," by Sir ARTHUR S. EDDINGTON, M.A., D.Sc., F.R.S.

"On radiometer action and the pressure of radiation," by MARY BELL, B.Sc., A.R.C.S., and S. E. GREEN, B.Sc., A.R.C.S., D.I.C., Imperial College of Science and Technology.

"The wet-and-dry-bulb hygrometer: the relation to theory of the experimental researches of Awbery and Griffiths," by F. J. W. WHIPPLE, M.A., Sc.D., F.Inst.P., Kew Observatory.

"The control of ignition-coil discharge characteristics," by G. I. FINCH, M.B.E., and R. W. SUTTON, Imperial College of Science and Technology.

"The temperature coefficient of the Weston standard cell," by P. VIGOUREUX and S. WATTS, National Physical Laboratory.

February 3, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

K. Rangadhama Rao, M. A. Elsherbini, Walter Gasson, Ernest Cuthbert Atkinson, Henry Rottenburg, D. R. Bhawalkar and John Hewitt Jellett Poole were elected to Fellowship of the Physical Society.

The President announced that P. S. Nilakantan and V. N. Dani had been elected to Student Membership of the Society.

The following papers were read:

"Relations between the combination coefficients of atmospheric ions," by F. J. W. WHIPPLE, M.A., Sc.D., F.Inst.P., Kew Observatory. (Read in title only.)

"The crystalline state of thin spluttered films of platinum," by Prof. G. P. THOMSON, F.R.S., NORMAN STUART, B.Sc., and C. A. MURISON, M.A., Imperial College of Science and Technology.

"Weekly measurements of upper-atmospheric ionization," by Prof. E. V. APPLETON, M.A., D.Sc., F.R.S., and R. NAISMITH, A.M.I.E.E., King's College, London.

"An automatic recording method for wireless investigations of the ionosphere," by J. A. RATCLIFFE, M.A., and E. L. C. WHITE, Cavendish Laboratory, Cambridge.

February 17, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Peter Kapitza, Ralph Stanley Chambers and Roy Witty were elected to Fellowship of the Society.

The President announced that Frederick Henry George Pitt had been admitted to Student Membership of the Society.

The following papers were read:

"The transmission of heat through fabrics," by M. C. MARSH, M.A., B.Sc., F.Inst.P., Wool Industries Research Association.

"A compact electromagnet for general purposes," by L. F. BATES, Ph.D., F.Inst.P., Reader in Physics, and B. J. LLOYD-EVANS, M.Sc. (Eng.), M.I.Mech.E., University College, London.

"On the spurious ring exhibited by fluorescent screens," by J. V. HUGHES, A.R.C.S., B.Sc.

"The direct recording of relative intensities by means of a microphotometer," by N. THOMPSON, B.Sc., The University, Sheffield.

A demonstration of short-wave radio apparatus was given by Dr W. L. YATES FISH, University College, London.

March 3, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

In the lecture theatre of the Western Electric Company, Ltd., Bush House, Kingsway, W.C. 2.

The President announced that L. F. Berry had been admitted to Student Membership of the Society.

A demonstration of the artificial larynx was given by Major GERALD JACQUES, M.I.E.E., of the Western Electric Co., Ltd.

By the courtesy of the Western Electric Co., Ltd., cinema films concerned with sound-recording and allied subjects were shown.

March 17, 1933.

Annual general meeting.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

The Minutes of the previous Annual General Meeting were read and accepted as correct.

The reports of the Council and Hon. Treasurer and the accounts were adopted.

The Officers and Council for 1933–1934 and the Auditors were elected.

Votes of thanks were accorded to the retiring Officers and Council and to the Governors of the Imperial College of Science and Technology.

Ordinary meeting.

William Frederick Floyd, Leonard George Holden Huxley and Edmund Ramsay Wigan were elected to Fellowship of the Society.

The following presentations to the joint library were announced from the Chair as having been received since the last meeting; the thanks of the Society were accorded to the donors.

From Mr A. Warren:

THOMSON, Sir WILLIAM. *Popular Lectures and Addresses.* Vol. I.

LARMOR, Sir JOSEPH. *Aether and Matter.*

FOURIER, JOSEPH. *The Analytical Theory of Heat.*

HAVELOCK, T. H. *The Propagation of Disturbances in Dispersive Media.*

Reprints from the *Bulletin of the Bureau of Standards.*

From Mr D. Oliver:

Journal of the Institution of Electrical Engineers. Vols. 33–54 (less 47).

From Sir Richard Paget:

About 500 *reprints of papers from the Bell Telephone Laboratories, New York.*

Gifts of missing parts from the runs of certain periodicals were announced from Major E. O. Henrici and Miss Mary Waller.

The following papers were read:

"A method for the determination of the thermal conductivities of rocks," by H. A. NANCARROW, B.Sc., A.Inst.P.

"A note on the Kerr cell," by E. E. WRIGHT, B.Sc.

"Tables to facilitate the calculation of the temperature-distribution in a cylinder," by H. A. NANCARROW, B.Sc., A.Inst.P.

"An experiment bearing on Talbot's bands," by the late A. C. G. BEACH, B.Sc., A.Inst.P.

April 7, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Bruce Chalmers and Arthur Joseph Woodall were elected to Fellowship of the Society.

It was announced that the Council had elected E. G. Jones, F. J. Martin and P. C. Sethi to Student Membership of the Society.

The following papers were read:

"The diffraction of X-rays by liquid sulphur," by A. H. BLATCHFORD, M.Sc., University of Reading.

"The hyperfine structure of perturbed series," by E. GWYNNE JONES, Imperial College of Science and Technology.

"Quartz as a standard for accurate lattice-spacing measurements," by A. J. BRADLEY, Ph.D., and A. H. JAY, M.Sc., University of Manchester.

"The thermal conductivity of water," by L. H. MARTIN, Ph.D., and K. C. Lang, M.A., M.Sc., University of Melbourne.

May 5, 1933.

The President, Prof. A. O. Rankine, O.B.E., D.Sc., F.Inst.P., in the Chair.

Syed Mehdi Ali and George Arthur Sutherland were elected to Fellowship of the Society.

The President announced that a new seal, designed by Mrs Mary Gillick, an illustration of which is shown herewith, and press had been presented to the Society by the Honorary Treasurer, Mr R. S. Whipple. The thanks of the Society were ordered to be presented to Mr Whipple for his generous gift.

(Half size)

A paper on "The measurement of visual sensations," was read by N. R. Campbell, Sc.D., F.Inst.P., and followed by an extensive discussion in which the following took part: Dr R. T. Beatty, Mr R. J. Bartlett, Mr J. Guild, Dr W. D. Wright, Mr T. Smith, Dr J. H. Shaxby, Major J. L. P. Macnair, Capt. C. W. Hume, Dr J. O. Irwen, The Rev. R. S. Maxwell, Dr R. A. Houstoun, and Dr L. F. Richardson.

The following papers were read:

"The measurement of the viscosity of a molten metal by means of an oscillating disc," by V. H. Stott, M.Sc., National Physical Laboratory, Teddington.

"Two simple methods of absolute measurement of electrical resistance," by H. R. Nettleton, D.Sc., Lecturer in Physics, Birkbeck College, and E. G. Balls, M.C., B.Sc., A.I.C., Research Student, Birkbeck College.

May 19, 1933.

The President, Prof. A. O. Rankine, O.B.E., D.Sc., F.Inst.P., in the Chair.

L. D. J. A. Dunoyer, Cecil Ernest Eddy, George Charles Eltenton, John Joseph McHenry and Ronald Leslie Moore were elected to Fellowship of the Society.

The following papers were read:

"Interference tones in superheterodyne receivers," by W. F. Floyd, B.Sc.

"A method of measuring the specific heats of poor conductors," by W. G. Marley, M.Sc.

"The demonstration of eddy currents in conductors of various shapes," by D. Brown, Ph.D., Auckland University College, New Zealand.

"The absence of fine structure in the arc spectrum of silver," by S. Tolansky, Ph.D., A.Inst.P.

"Thermomagnetic hysteresis in steel," by W. Y. Chang, M.S. (Yenching), and William Band, M.Sc., Professor of Physics, Yenching University, Peiping, China.

June 2, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Geoffrey Ghey was elected to Fellowship of the Society.

An illustrated account and demonstrations of recent developments in infra-red photography were given by Mr OLAF BLOCK, F.I.C.

The following papers were read:

"Observations on the intensity of low-frequency sounds close to a metal air-screw," by C. F. B. KEMP, A.R.C.S., B.Sc., A.Inst.P.

"The visibility of objects in a searchlight beam," by W. M. HAMPTON, Ph.D., F.Inst.P.

June 16, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

T. T. Thomas was elected to Fellowship of the Society.

The tenth Duddell Medal was presented to Prof. Wolfgang Gaede.

The eighteenth Guthrie Lecture was delivered by Prof. M. SIEGBAHN of the University of Upsala, who took as his subject "Studies in the Extreme Ultra-Violet and the Very Soft X-ray Region."

July 7, 1933.

The PRESIDENT, Prof. A. O. RANKINE, O.B.E., D.Sc., F.Inst.P., in the Chair.

Geoffrey Builder was elected to Fellowship of the Society.

The following presentations to the joint library were announced from the Chair as having been made since the last meeting; the thanks of the Society were accorded to the donors.

PETERS, S. P. *Meteorological Office. Geophysical Memoirs No.* 56, *Professional Notes, Nos.* 59 *and* 64. Presented by the author.

EDGCUMBE, K. and OCKENDEN, F. E. J. *Industrial Electrical Measuring Instruments.* Presented by the authors.

GLADSTONE, J. H. and TRIBE, A. *The Chemistry of the Secondary Batteries of Planté and Faure.* Presented by Mr B. M. Neville, A.Inst.P.

The following papers were read:

"Conditions for securing accuracy in spectrophotometry," by F. TWYMAN, F.Inst.P., F.R.S., and G. F. LOTHIAN, B.A.

"Studies in interferometry.—II. The construction, testing and use of reflection echelons for the visible and ultra-violet regions," by W. EWART WILLIAMS, M.Sc.

"Two methods of ionospheric investigation," by E. V. APPLETON, M.A., D.Sc., F.R.S.

"A high-temperature X-ray camera for precision measurements," by A. H. Jay, M.Sc.

"The intensities of bands in the spectrum of boron monoxide," by A. Elliott, Ph.D., D.Sc.

"Pressure effects in the spectra Xe I and Xe II," by J. F. Heard, Ph.D.

"Hyperfine structure in the spark spectrum of cadmium," by E. Gwynne Jones.

A demonstration of a new capacity-meter was given by Mr W. L. Beck.

Visit to Cambridge, July 22, 1933.

Through the kindness of Prof. Lord Rutherford and the Cambridge Instrument Company, Ltd., a visit was paid to the works of the Company and to the Cavendish Laboratory. Visitors were entertained to lunch at the Company's works and to tea in the Laboratory.

A science meeting was held at the Laboratory and after an introductory address by Prof. Lord Rutherford the following papers were read:

"Artificial transmutations by high-speed protons," by E. T. S. Walton, Ph.D., and P. I. Dee, M.A.

"Artificial transmutations by high-speed protons," by M. L. Oliphant, Ph.D.

"The magnetic analysis of long-range α particles," by W. B. Lewis, B.A.

Demonstrations were arranged by Prof. Kapitza, F.R.S., Dr Walton and Mr Dee.

REPORT OF COUNCIL FOR THE YEAR ENDING FEBRUARY 28, 1933

MEETINGS

During the period covered by the Report 13 Ordinary Science Meetings were held at the Imperial College of Science and Technology.

At these meetings 56 papers were presented and 4 demonstrations given.

On May 6 a meeting was held at the Physiological Laboratories, University College, London, and a series of demonstrations were given by Professor A. V. Hill, F.R.S., and the staff, followed by a lecture by Professor Hill.

On June 3 a Discussion on Vision was held at the Imperial College of Science and Technology to which 28 papers were contributed.

On June 11 members of the Society and their friends visited Nottingham University College at the invitation of Professor Brose; at this meeting 6 papers were read, and the contributors were Professor J. S. Townsend, F.R.S., of Oxford and members of the staff of the Physics Department of Nottingham University College.

A lecture on "The Manufacture of Optical Glass" was delivered on October 7 by Dr J. W. French, F.Inst.P.

THE DUDDELL MEDAL

At the Annual Meeting on March 18, 1932, the Ninth Duddell Medal was presented to Professor C. T. R. Wilson, F.R.S. The Council has awarded the Tenth Duddell Medal to Dr Wolfgang Gaede.

GUTHRIE LECTURE

Professor Max Planck delivered the Seventeenth Guthrie Lecture on June 17, 1932, the subject being "The Concept of Causality."

SPECIAL REPORT

The report on "Band Spectra of Diatomic Molecules," by W. Jevons, D.Sc., was issued during November 1932.

OBITUARY

The Council records with deep regret the deaths of Mr A. C. G. Beach, Mr Edwin Edser, Mr St George Lane Fox-Pitt, Mr William Francis, Mr H. Chapman Jones, Professor R. Ll. Jones, Mr J. Saynor, Mr W. S. Seaton, Sir Richard Threlfall, Mr G. Fergus Wood.

EXHIBITION

The Twenty-Third Annual Exhibition was held on January 3, 4 and 5, 1933, at the Imperial College of Science and Technology by courtesy of the Governing Body.

The Research and Experimental Section included exhibits from 25 sources. Trade exhibits were shown by 83 firms. Discourses were given by A. Ferguson, M.A., D.Sc., F.Inst.P., on "Surface Tension and its Measurement"; by R. A. Watson Watt, B.Sc., A.M.I.E.E., F.Inst.P., on "Cathode Ray Oscillography"; and by F. Hope-Jones, M.I.E.E., F.R.A.S., on "Time Measurement; Old and New."

REPRESENTATIVES ON OTHER BODIES

The representation of the Society on the Committee of Management of *Science Abstracts* has been increased from two to four. The representatives are Dr A. Ferguson, Dr D. Owen, Professor G. F. J. Temple and Professor G. P. Thomson, the last named two being the additional representatives.

Dr D. Owen and Dr E. Griffiths were appointed to represent the Society on the Board of the Institute of Physics.

Mr E. F. Fincham was nominated the representative of the Society on the Joint Committee of the Institute of Ophthalmic Opticians and the Association of Wholesale and Manufacturing Opticians.

Dr J. H. Brinkworth, Dr Allan Ferguson, Dr J. S. Anderson, Professor A. F. C. Pollard and Dr J. S. G. Thomas are the representatives of the Society on the Joint Library Committee.

UNION WITH THE OPTICAL SOCIETY

The outstanding event of the year has been the union of the Optical Society with the Physical Society of London. This step was desirable on various grounds, and after full consideration of the financial, legal and other considerations involved, the Councils of the two Societies unanimously decided to recommend an amalgamation. This recommendation was put to the test of a post-card vote and was carried by an overwhelming majority. The necessary legal business has been successfully carried through, and the fusion of the two Societies under the title of "The Physical Society" has been completed. The Physical Society enters upon this term of its existence with a largely extended membership and correspondingly increased obligations. Those activities which are specially characteristic of the parent Societies will be consistently continued. The Guthrie Lecture and the Thomas Young Oration will be delivered at regular intervals; the *Proceedings* will be issued in six parts per annum instead of five and the Council has in contemplation the production at regular intervals (probably annually) of a series of reports on the state of physical science, which will include surveys of the progress in optical and allied matters.

INTERNATIONAL DECIMAL CLASSIFICATION

The Council decided to adopt the International Decimal Classification system for the indexing of the papers published in the *Proceedings*. Commencing with Part I, of volume 45 (January 1933), the appropriate index numbers are printed at the head of each paper; they are also included in the Bulletins.

SCIENCE ABSTRACTS

The Committee of Management of *Science Abstracts* has for some time past had under consideration the enlargement of the index and indeed the complete re-organization of the existing system of indexing. This re-organization has now been carried out and the volume of *Science Abstracts* (Section A) for 1932 will be indexed under the new system. Arrangements have been made by which the interval between the date of publication of a paper and its appearance in abstract form in *Science Abstracts* will be considerably lessened.

LIBRARY

During the year considerable progress has been made by the Joint Library Committee set up some time ago by the Institute of Physics, the Physical Society of London, and the Optical Society. The main part of the joint library is now housed in some rooms at the Institute of Physics which have been comfortably furnished for use as reading and writing rooms. These rooms were opened by Lord Rutherford in May 1932. A number of periodicals are already available for reference and a nucleus of textbooks and works of reference is also available.

MEMBERSHIP ROLL

	Total Dec. 31, 1931	Changes during 1932			Total Dec. 31, 1932
Honorary Fellows	9	—			9
Ordinary Fellows	773	Elected		33	
		Transferred from Optical Society		132	
		Student transfers ...		14	
				179	
		Deceased	11		
		Resigned or lapsed ...	40		
				51	
		Net increase		128	901
Students	60	Elected		18	
		Transferred from Optical Society		4	
				22	
		Trans. to Fellow ...	14		
		Resigned	14		
				28	
		Net decrease		6	54
Total Membership	842	Net increase		122	964

Note. The option of former members of the Optical Society to transfer their membership to the Physical Society does not expire until March 31, 1933.

REPORT OF THE HONORARY TREASURER

THE accounts for the year ended December 31st, 1932 show an excess of Expenditure over Income of £496. 1*s*. 9*d*.

It will be seen that an important change has been made in the form of the Accounts, in that the item "Stock of Publications," which has always headed the Income and Expenditure Account, has been omitted. It is difficult to determine the commercial value of the Proceedings of a Scientific Society, and for this reason the Council has decided that, in future, a carefully estimated value of the stock will be shown as a footnote on the Balance Sheet. It has also been decided to transfer from the Life Compositions Fund to the Income and Expenditure Account the money which has been standing to the credit of deceased members: this amount is no longer a liability against the Society.

A heavy expenditure was incurred by the Society in the publication of two Reports—"The Report on Band Spectra" by Dr W. Jevons, and the "Discussion on Vision," which contains the papers presented to the Joint Meeting of the Optical and Physical Societies held on June 3rd, 1932.

The greatly increased expenditure on Science Abstracts as compared with that of 1931 is due to the expansion of the Index and the acceleration of the publication of the Abstracts.

It has been decided not to publish separate accounts of the Optical Society for 1932. The detailed accounts may be seen by any interested Fellow at the office of the Society. The assets and liabilities of the Optical Society at December 31st, 1932, have been included in the Balance Sheet. These assets include the stock of publications to the value of £489. 18*s*. 0*d*. (shown as a footnote on the Balance Sheet) and £750 $3\frac{1}{2}$ % War Loan. The expenses connected with the amalgamation of the Optical Society with the Physical Society of London amounted to £114. 7*s*. 7*d*. The thanks of the Fellows of the two Societies are due to Major Henrici, the late Treasurer of the Optical Society, who acted as Trustee of the Optical Society during the transfer of the accounts. The Council of the Physical Society has taken over the Trusteeship of the Optical Convention 1926.

£1400 War Loan 1929/47 Inscribed Stock was converted into $3\frac{1}{2}$ % War Loan Inscribed Stock.

The Society's investments have been valued at market prices on December 31st, 1932, through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank.

(*Signed*) ROBERT S. WHIPPLE
Honorary Treasurer

March 3rd, 1933

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1932

1931 £ s. d.	Expenditure	£ s. d.	£ s. d.
	To		
239 0 0	Science Abstracts		564 0 0
	Ordinary Publications:		
1315 2 8	"Proceedings"	1176 16 4	
78 13 2	"Bulletin" and Notices	102 3 5	
137 16 9	Editorial and General Expenses	169 11 4	
			1448 11 1
113 15 2	Postage on Ordinary Publications		121 8 8
	Editing, Printing and Distributing "Discussion on Vision"	567 19 4	
	Less Amount charged to Optical Society	145 3 11	
			422 15 5
	Editing, Printing and Distributing "Report on Band Spectra"		678 12 8
37 9 1	Expenses at Meetings		44 7 10
	Exhibition Account:		
664 5 11	Printing, Electrical and Labour charges	727 15 4	
67 6 0	Optical Society Exhibition Account	44 4 4	
180 13 1	Contribution towards Administration Expenses of Exhibition	114 2 2	
			886 1 10
6 7 0	Periodicals and Library		6 2 6
	Administration Expenses:		
149 11 3	Institute of Physics	325 17 10	
105 15 5	Office Expenses	165 0 1	
			490 17 11
	Publicity		20 7 3
	Expenses of amalgamation with the Optical Society	146 17 9	
	Less Amount charged to Optical Society	32 10 2	
			114 7 7
20 0 0	Honorarium to Guthrie Lecturer		26 5 0
294 4 2	*Printing and Publishing "Discussion on Audition"*		
87 15 7	*Balance, being excess of Income over Expenditure*		
£3497 15 3			£4823 17 9

1931 £ s. d.	Income	£ s. d.	£ s. d.
	By		
	Subscriptions:		
	Entrance Fees during 1932	27 6 0	
1327 2 2	Fellows*	1339 13 7	
7 7 0	(Voluntary†)	26 6 0	
18 7 6	Students	19 19 0	
102 17 0	For "Science Abstracts" and Advance Proofs	97 15 0	
			1510 19 7
	Transfer from Life Compositions Fund of amounts paid by Fellows now deceased		760 10 0
626 11 9	Sales of Publications		633 15 8
194 5 10	Advertisements in "Proceedings"		129 0 2
	Dividends from Investments and Bank Interest	240 19 3	
	Add Income Tax refunded and claimed	36 9 6	
		277 8 9	
308 19 0	*Less* Transfer to Duddell Memorial Fund	20 0 0	
			257 8 9
912 5 0	Exhibitors' Payments on account of Exhibition		886 1 10
	Royal Society Grant for Publications		150 0 0
	Balance, being excess of Expenditure over Income, carried forward to Accumulated Fund		496 1 9
£3497 15 3			£4823 17 9

* Eighty-eight Fellows paid reduced subscriptions by the arrangement with the Institute of Physics, the total rebate being £31. 9*s*. 1*d*.

† Voluntary subscriptions are subscriptions paid by Fellows who compounded for the low sum of £10.

BALANCE SHEET AT 31st DECEMBER, 1933

LIABILITIES

	£ s. d.	£ s. d.
Accumulated Fund:		
As per last Balance Sheet	1730 15 6	
Less Stock of Publications at 1st January, 1932	747 0 0	
	983 15 6	
Balance brought forward from Income and Expenditure Account	496 1 9	
	487 13 9	
Add Transfer from Optical Society	624 5 6	
Add Increased value of Investments	1012 0 0	
		2123 19 3
Life Compositions:		
As per last Balance Sheet	2384 0 0	
Less Transfer to Income and Expenditure Account of amounts paid by Fellows now deceased	760 10 0	
	1623 10 0	
Add Amount transferred from Optical Society	94 10 0	
		1718 0 0
Duddell Memorial Trust Fund:		
As per last Balance Sheet	410 12 9	
Add Special Bonus on War Loan conversion	4 0 0	
Add Increased value of Investments	12 0 0	
		426 12 9
W. F. Stanley Trust Fund:		
As per last Balance Sheet	155 0 0	
Less Decreased value of Investments	27 0 0	
		128 0 0
A. W. Scott Bequest		250 0 0
Sundry Creditors: Physical Society	2341 5 0	
Optical Society	252 7 5	
		2593 12 5
Subscriptions paid in advance:		
Members	36 11 1	
Publications	194 14 5	
		231 5 6
Optical Convention, 1926, *Trust Account*		25 5 5
		£7496 15 4

ASSETS

	£ s. d.	£ s. d.	£ s. d.
Investments at Market Value on December 31, 1932:			
£1500 Consolidated Stock 2½%	1110 0 0		
£1000 War Loan 3½% Inscribed "A" Account	990 0 0		
£750 War Loan 3½% (from Optical Society)	742 0 0		
£400 War Loan 3½% Inscribed "B" Account	396 0 0		
£650 Funding Loan 4% 1960/90	709 0 0		
£500 India 3½% Stock	440 0 0		
£254. 2*s*. 9*d*. New South Wales 5% Stock 1935/55	257 0 0		
£211 London County Consolidated 4½% Stock	230 0 0		
£400 Lancaster Corporation 3% Redeemable Stock	376 0 0		
£399 London Midland and Scottish Railway 4% Debenture Stock	360 0 0		
£1000 London Midland and Scottish Railway 4% Preference Stock	360 0 0		
£500 London and North-Eastern Railway 4% Debenture Stock	405 0 0		
£150 Southern Railway 5% Debenture Stock	173 0 0		
£300 Southern Railway Preferred Ordinary Stock	84 0 0		
£442 Southern Railway Deferred Ordinary Stock	44 0 0		
			6676 0 0
Dividends due from Investments			36 19 3
Inland Revenue—Income Tax claimed for 1932			25 15 5
Subscriptions due			25 14 0
Sundry Debtors: Physical Society	291 1 7		
Optical Society	50 4 7		
			341 6 2
Cash at Bank: Physical Society	185 19 7		
Optical Society	200 15 5		
			386 15 0
Cash in hand Physical Society	17 2		
Optical Society	3 8 4		
			4 5 6
			£7496 15 4

Stock of publications at 31st December, 1932. At Honorary Treasurer's valuation:

Physical Society	1167 13 0
Optical Society	489 18 0
	£1657 11 0

ROBERT S. WHIPPLE, *Honorary Treasurer.*

We have audited the above Balance Sheet and have obtained all the information and explanations we have required. We have verified the Bank Balances and the Investments. In our opinion such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the Society's affairs according to the best of our information and the explanations given to us and as shown by the books of the Society.

KNOX, CROPPER & CO.,
Chartered Accountants

SPENCER HOUSE, SOUTH PLACE, E.C. 2
3rd March 1933.

LIFE COMPOSITIONS FUND AT DECEMBER 31ST, 1933

	£	s.	d.
65 Fellows paid £10	650	0	0
2 Fellows paid £15	30	0	0
15 Fellows paid £21	315	0	0
1 Fellow paid £30	30	0	0
22 Fellows paid £31. 10s.	693	0	0
	£1718	0	0

W. F. STANLEY TRUST FUND (FOR THE "BULLETIN")

	£	s.	d.		£	s.	d.
£300 Southern Railway Preferred Ordinary Stock	84	0	0	Carried to Balance Sheet	128	0	0
£442 Southern Railway Deferred Ordinary Stock	44	0	0				
	£128	0	0		£128	0	0

DUDDELL MEMORIAL TRUST FUND

Capital

	£	s.	d.		£	s.	d.
£400 War Loan 3½% Inscribed Stock	396	0	0	Carried to Balance Sheet	396	0	0

Revenue

	£	s.	d.		£	s.	d.
Balance at 31st December, 1931	26	12	9	Honorarium to Medallist	20	0	0
Special Bonus on War Loan Conversion	4	0	0	Balance carried to Balance Sheet	30	12	9
Dividends	20	0	0				
	£50	12	9		£50	12	9

OPTICAL CONVENTION, 1926, TRUST ACCOUNT

	£	s.	d.		£	s.	d.
Balance at 31st December, 1931	173	18	1	Return of 10% of Guarantee Fund	170	3	3
Sales of publications	18	0	10	Loss on sale of investment	2	10	3
Dividends	6	0	0	Balance carried to Balance Sheet	25	5	5
	£197	18	11		£197	18	11

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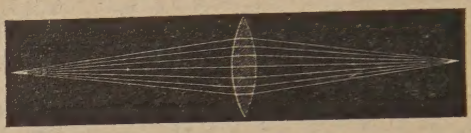

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